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13. ABSTRACT (Maximum 200 words) Studies of the thermal and photon-induced surface chemistry of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe) on GaAs(100) substrates under ultrahigh vacuum conditions have been performed for substrate temperatures in the range of 123 K to 473 K. Results indicate that extremely efficient conversion of admixtures of DMTe and DMCd to CdTe can be obtained using low power (5 - 10 mJ cm ⁻²) 193 nm laser pulses at substrate temperatures of 123 K. Subsequent annealing at 473 K produces an epitaxial film. Given the similar electronic structure of other II-VI metal alkyls, such as dimethyl mercury, zinc, and selenium, it is believed that laser induced surface chemical epitaxy is suitable for producing patterned deposits of II-VI quantum well structures. manometers				
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**LASER INDUCED SURFACE CHEMICAL EPITAXY:
A NOVEL THIN FILM DEPOSITION TECHNIQUE**

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TABLE OF CONTENTS

Section	Page
1 INTRODUCTION	1-1
2 EXPERIMENTAL APPROACH	2 -1
2.1 Experimental Apparatus	2 -1
2.2 X-Ray Photoelectron Spectroscopy	2 -2
3 RESULTS	3-1
3.1 Thermal Surface Chemistry of DMCd, DMTe and DMCd/DMTe Overlayers	3-1
3.2 Photon Induced Surface Chemistry and Deposition of CdTe Thin Films	3-10
4 CONCLUSIONS	4-1
4.1 Summary	4-1
4.2 Recommendations	4-2
5 REFERENCES	5-1
6 PROGRAM MANAGEMENT	6-1
6.1 Key Personnel	6-1
6.2 Presentations	6-2
6.3 Publications	6-3



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1 INTRODUCTION

Thermal and photon-induced deposition processes involving organometallic precursor species are currently being investigated for II-VI and III-V compound semiconductors.¹ These processes provide the potential for reduced growth temperatures and increased process flexibility. Illustrations include reduced pressure laser-assisted chemical vapor deposition (LCVD) of CdTe² and ultra high vacuum (UHV) metalorganic molecular beam epitaxy (MOMBE) of GaAs.³ These relatively new deposition processes raise important questions concerning chemical mechanisms which must be answered if the processes and materials they produce are to be optimized.

This report describes experimental studies of the thermal and photon-induced surface reactions of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe). The objectives of these studies were to provide an understanding of the underlying chemical and physical processes and to explore a novel approach to CdTe heteroepitaxy identified as Laser-Induced Surface Chemical Epitaxy (LSCE). The essential features of LSCE as applied to CdTe epitaxy involve: coadsorption of DMCd and DMTe on a GaAs (100) substrate at 123 K; UV laser irradiation at 193 nm to produce a laser initiated reaction between the adspecies and a short thermal anneal (~ 160 s) at 473 K to order the deposit. Using this approach epitaxial CdTe thin films on the order of 10 nm to 20 nm have been produced.^{4,5} Figure 1.1 presents a schematic of this process.

This research focuses on CdTe heteroepitaxy because of the importance of this material in electro-optical systems.⁶ DMCd and DMTe were selected as the precursor species because of their inherent scientific interest. The gas phase photochemistry of DMCd and DMTe has been extensively investigated; these molecules are known to undergo single photon dissociation to produce ground state metal atoms.⁷⁻⁹ This behavior contrasts with that of trimethyl gallium and trimethyl arsenic which dissociate in the gas phase via a multiphoton excitation process.¹⁰ Thus, fundamental questions addressed in this study

are: i) How do DMCd and DMTe, either as pure or coadsorbed species, interact on the surface? and ii) Is this interaction such that single photon (as opposed to multiphoton) processes can be used to produce epitaxial CdTe thin films?

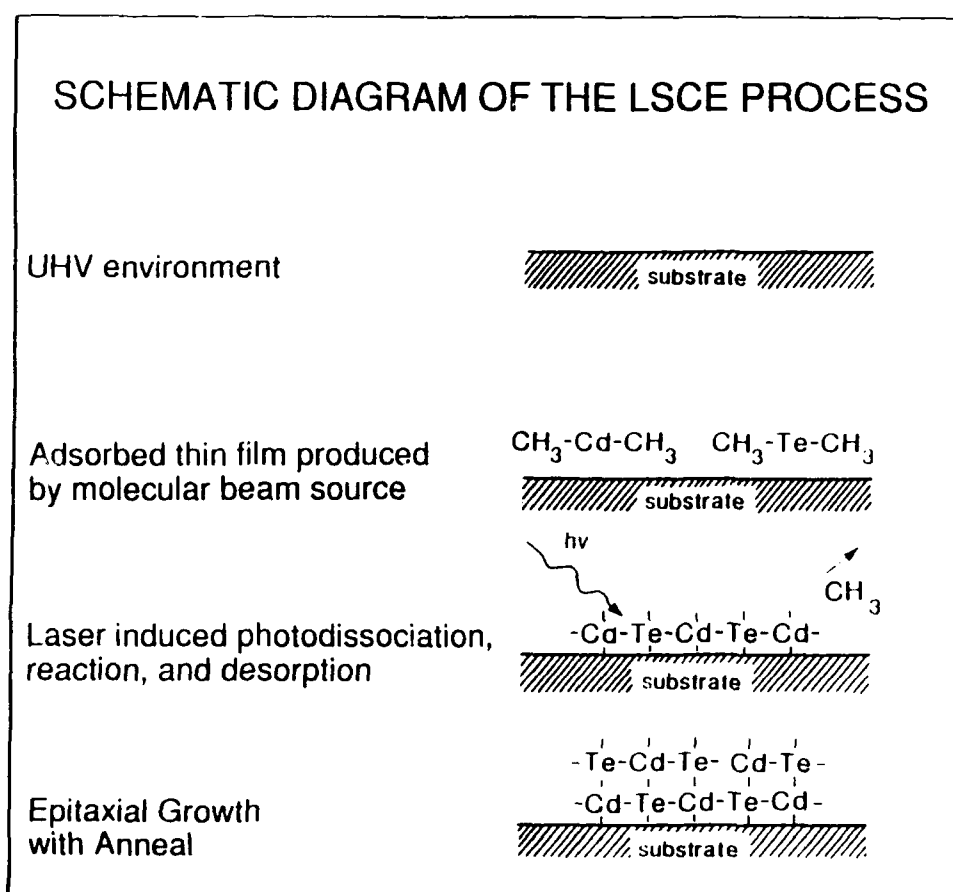


Figure 1.1. Schematic of the LSCE process.

2. EXPERIMENTAL APPROACH

2.1 Experimental Apparatus

The apparatus used in these studies is shown in Figure 2.1. It consists of a turbomolecular pumped, liquid nitrogen trapped Ultrahigh Vacuum (UHV) reaction cell interfaced to an ion/sublimation pumped UHV analysis chamber. The diagnostics used in these studies were X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Samples were transferred between chambers using a Vacuum Generators linear motion feedthrough with sample heating (1200 K) and cooling (123 K) capabilities. An effusive molecular beam doser was used to expose the sample to DMCd and/or DMTe. For the sample-source geometry used here, the angular distribution of the effusive beam produced only a nominal 10% variation in exposure over the area of the sample ($\sim 1 \text{ cm}^2$). Proper sample positioning in the beam was determined by observing the interference pattern produced by a thick adlayer.

Photon-induced processes were studied by irradiating the adlayer with ultraviolet photons produced by a Questek excimer laser. These were introduced into the deposition chamber through a Conflat mounted MgF_2 window (Harshaw). The wavelengths used in these studies were 193 nm, 248 nm, and 351 nm. The laser energy fluence, controlled using a simple beam expander, ranged from 0.3 mJ cm^{-2} per pulse to 6 mJ cm^{-2} per pulse to minimize the effects of surface heating ($< 3 \text{ K}$ to 60 K).¹¹

The GaAs (100) samples used in these experiments were p-type electronic grade single crystal substrates provided by Litton. In situ sample cleaning involved Ar^+ ion etching at 1 kV until no trace of oxygen could be detected using XPS. This was followed by annealing at 850 K to produce a gallium rich surface and restore surface order as observed by LEED.¹²

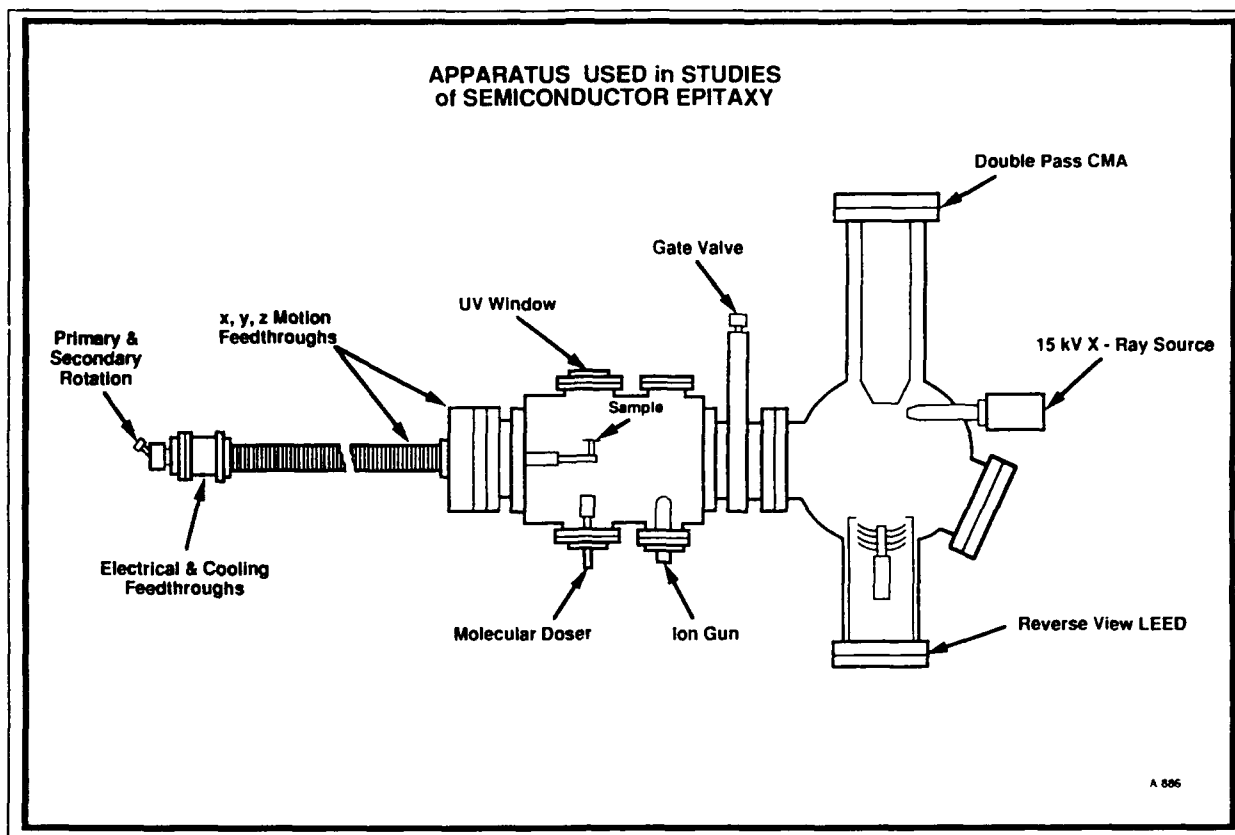


Figure 2.1 Cross sectional view of the deposition and analysis system.

The DMCd and DMTe were obtained from Alfa and were purified using a series of freeze-thaw cycles.

2.2 X-ray Photoelectron Spectroscopy

XPS analyses were performed using a PHI 15 kV Mg K_{α} X-ray source and a PHI double pass cylindrical mirror electron energy analyzer (15-255 GAR) with angular resolution capabilities. The analyzer was operated at a pass energy of 25 eV and calibrated using the Au $4f_{7/2}$ peak at 83.8 eV. The XPS peak binding energies observed using this system were reproducible to ± 0.2 eV. No sample charging effects were observed except in the limit of very thick overlayers (i.e. > 20 nm). Data was acquired using a PHI data processing board and analyzed using Spectra Calc software.

In XPS, the sample to be studied is exposed under vacuum to soft X-rays which cause photoelectrons to be ejected from atoms in the surface and near surface layers. These photoelectrons originate from core and valence levels of the atoms and are analyzed in terms of the binding energies of these levels. These data provide information on the identity of the atoms and, because the atomic levels are sensitive to the chemical environment of the atoms, on their chemical state. Electron binding energies and differences in electron binding energy associated with different chemical state of a given atomic species (i.e. chemical shifts) have been extensively studied and catalogued.¹³⁻¹⁶

This study focuses on XPS analyses of Cd and Te adspecies on GaAs (100) substrates. For the annealed GaAs substrate, Ga and As 3d_{5/2} peak binding energies of 18.8 eV and 40.8 eV, respectively, were observed throughout the experiment and are consistent with previously reported values.^{13,16} In the case of the Cd and Te adspecies, Table 2.1 shows reference values for the binding energies of the Cd and Te 3d_{5/2} peaks.

Table 2.1 Cd and Te XPS 3d_{5/2} Peak Binding Energies

3d _{5/2} Binding Energy (eV \pm 0.2 eV)		
<u>Species</u>	<u>Cd</u>	<u>Te</u>
Metal	404.6	572.6
Dimethyl-	405.8	574.9
CdTe	405.0	572.4

The values for CdTe were observed for CdTe epitaxial films deposited on GaAs in this study and are consistent with previously reported observations.¹⁶ Likewise, the values for DMCD and DMTE (physisorbed) were established in this investigation from measurements of pure, thick overlayers adsorbed at 123 K. The values for metallic Cd and Te were obtained from previously reported results.¹⁶ It is important to stress that although a Te 3d_{5/2} binding energy of

572.6 eV was observed in this study for DMTe adlayers annealed at 423 K, a condition which is likely to produce a metallic Te adlayer, the Cd $3d_{5/2}$ binding energy observed for similarly annealed DMCd adlayers was 405.1 eV. Based on room temperature measurements and ligand shift and electronegativity arguments,¹⁷⁻²¹ this species was previously identified by us as monomethyl-Cd.^{22,23}

In addition to the binding energy, the intensity of a given XPS peak is also of interest. The intensity of XPS peaks for species present on the surface at monolayer and lower coverages is directly proportional to surface coverage. In this study, calculational techniques developed by Madey et.al.²⁴ were used to determine the coverage from known values of the X-ray mass absorption coefficients, photoelectron cross section, and measured ratios of substrate and adspecies peak intensities (areas). For thicker films, similar techniques have been used to determine the deposit thickness.¹³ Based on ionic radii, a monolayer (1ML) surface coverage of DMCd or DMTe molecules was taken as $2.8 \times 10^{14} \text{ cm}^{-2}$. This is comparable to the value used for trimethyl gallium and trimethyl arsenic in studies of photon-assisted GaAs deposition.¹⁰

3 RESULTS AND DISCUSSION

3.1 Thermal Surface Chemistry of DMCd, DMTe, and DMCd/DMTe Overlayers

Figure 3.1 shows Cd $3d_{5/2}$ XPS peaks for DMCd adsorbed on the GaAs (100) surface at 123 K for Cd surface coverages of $0.7 \times 10^{14} \text{ cm}^{-2}$, $2.4 \times 10^{14} \text{ cm}^{-2}$, and $5.3 \times 10^{14} \text{ cm}^{-2}$. These coverages correspond to approximately 0.3 ML, 1 ML, and 2 ML, respectively. As the Cd surface coverage increases from the submonolayer to the multilayer regime, it may be seen that the binding energy shifts from 405.1 eV to 405.8 eV. The FWHM, however, remains approximately constant at 1.9 eV as the coverage increases.

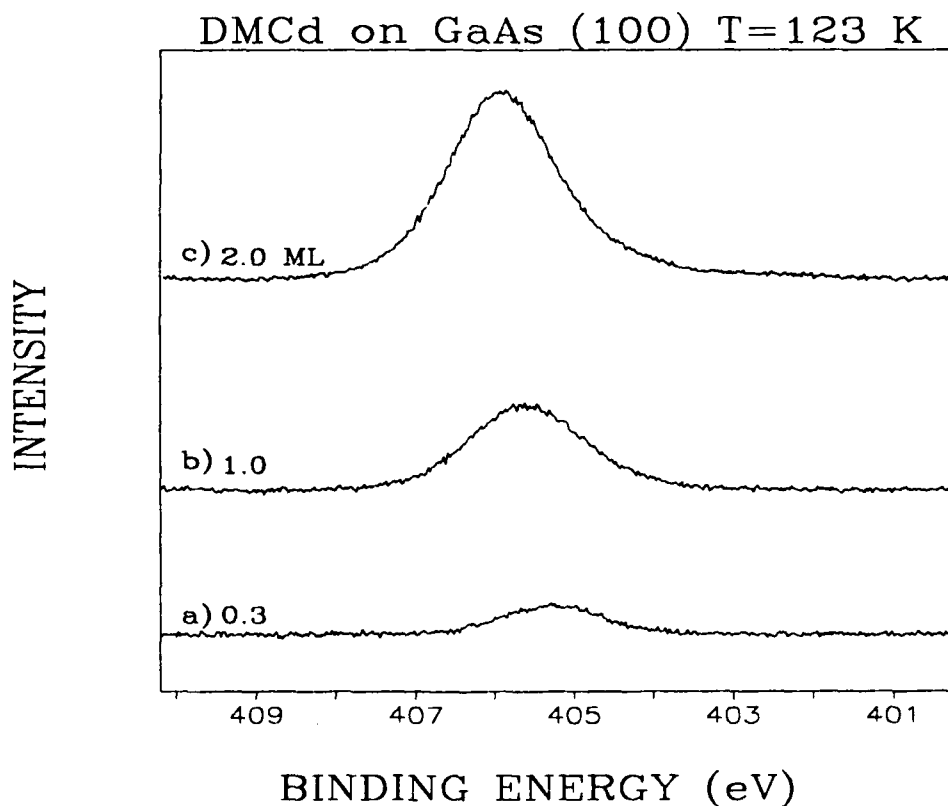


Figure 3.1. Cd $3d_{5/2}$ XPS Peaks For DMCd Adsorbed On The GaAs (100) Surface At 123 K For Cd Surface Coverages Of a) $0.7 \times 10^{14} \text{ cm}^{-2}$, b) $2.4 \times 10^{14} \text{ cm}^{-2}$, and c) $5.3 \times 10^{14} \text{ cm}^{-2}$.

The Cd $3d_{5/2}$ peak at 405.8 eV is attributed to physisorbed DMCD since increases in coverage up to approximately 40 ML (i.e. a condensed overlayer) produce no further changes in binding energy. The shift of the peaks to lower binding energy with decreasing surface coverage indicates that the adspecies-surface interaction involves chemisorption with coverage dependent electron transfer from the surface to the adspecies. This is consistent with the fact that DMCD, although having a fully saturated valence (fully paired d and s electrons), has three empty low lying Cd p orbitals which are available for accepting electrons from the surface. Whether or not the chemisorption process is dissociative can not be established from these data. As discussed later, however, the peak at 405.1 eV observed at the lowest coverages is comparable to that observed at 423 K where dissociative chemisorption almost certainly occurs.

Figure 3.2 shows Te $3d_{5/2}$ XPS peaks for DMTe adsorbed onto the GaAs surface at 123 K for Te surface coverages of 0.4 ML, 0.6 ML, and 1 ML. Here, in contrast to the case for DMCD, the binding energy remains essentially constant at 574.9 eV, while the FWHM increases with increasing coverage. This broadening, associated with the appearance of a shoulder on the low binding energy side of the peak, is attributed to the partial decomposition of the adspecies as a result of interactions between the adspecies and the Mg K_{α} X-rays rather than as a result of the adspecies - GaAs surface interaction. Evidence for this provided in Figure 3.3 which shows the enhancement of the shoulder with increased X-ray exposure. Thus, this broadening is considered to be an artifact of the analysis technique and not a result of the adspecies - surface interaction.

DMTe on GaAs (100) at 123 K

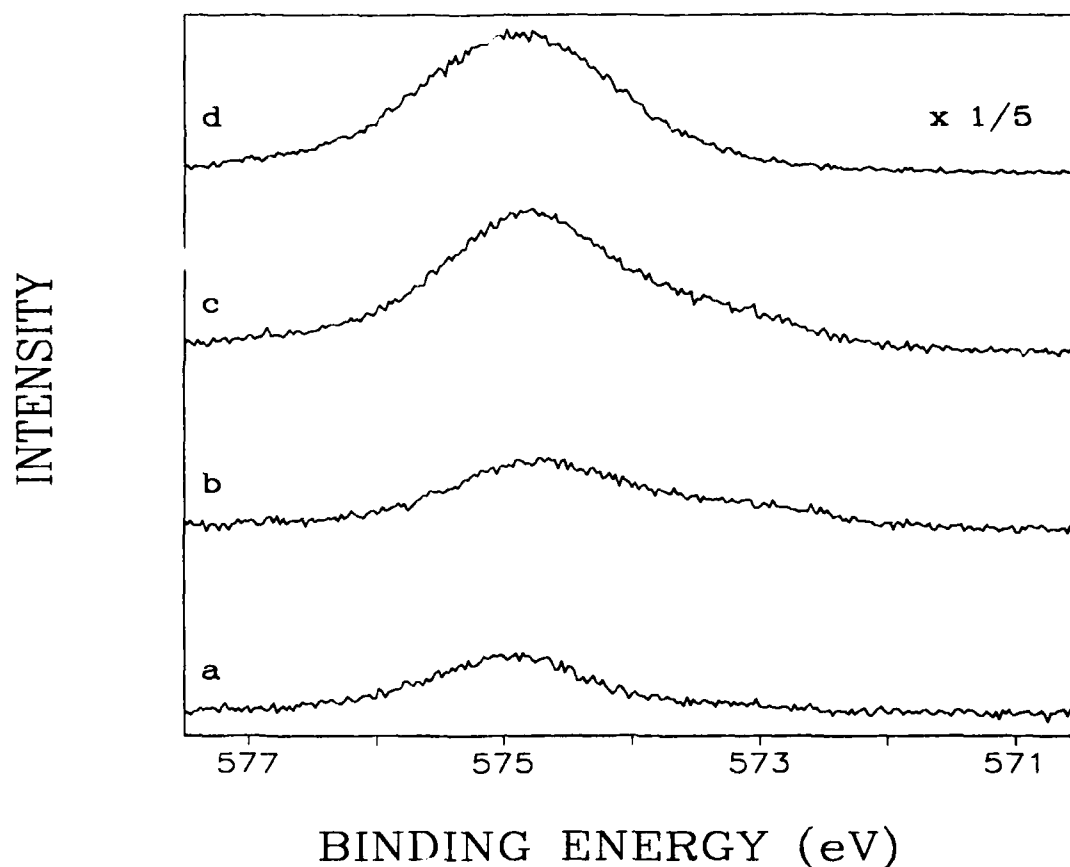


Figure 3.2. Te 3d_{5/2} XPS Peaks For DMTe Adsorbed On The GaAs (100) Surface At 123 K For Te Surface Coverages Of a) 0.3 ML, b) 0.6 ML, and c) 1 ML.

The Te 3d_{5/2} peak at 574.9 eV (1.8 eV FWHM), observed for submonolayer through multilayer coverages, is attributed to physisorbed DMTe. This is supported by the observation that increases in coverage up to 40 ML (i.e. a condensed overlayer) produce no further changes in binding energy. Thus, the dominant DMTe surface - interaction appears to involve physisorption over the entire coverage range. This is consistent with the fact that DMTe is a closed shell molecule which should interact only weakly, if at all, with the surface.

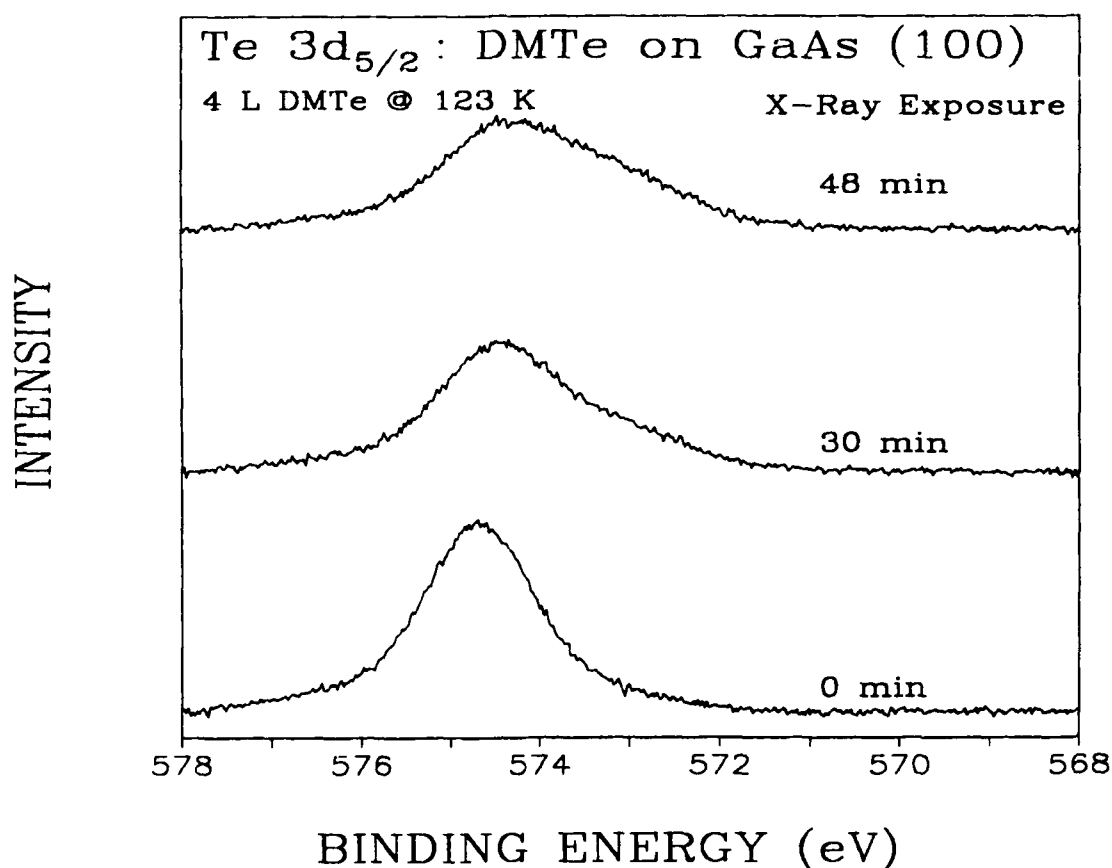


Figure 3.3. The Effect Of X-Ray Exposure On The Te 3d_{5/2} XPS Peak Shape

Figure 3.4 shows the C 1s XPS peaks corresponding to the Cd and Te 3d_{5/2} peaks shown, respectively, in Figures 3.1(c) and 3.2(c) (i.e. physisorbed adspecies). The signal-to-noise levels for these spectra are low due to the small C 1s cross section; however, two distinct peaks, one at 284.9 eV for physisorbed DMCd and one at 283.7 eV for physisorbed DMTe, are evident. The decrease in C 1s binding energy of 1.2 eV on going from DMTe to DMCd is consistent with the greater electronegativity of Te. Taking into account the relative cross sections of C, Cd, and Te obtained from condensed overlayers, the carbon-to-metal ratio for the peaks shown here is nominally 2 (1.9 for DMCd and 1.6 for DMTe). This is consistent with the assignment of the Cd and Te XPS peaks to physisorbed adspecies. The slightly lower ratio for Te may be due to the Mg K_α X-ray

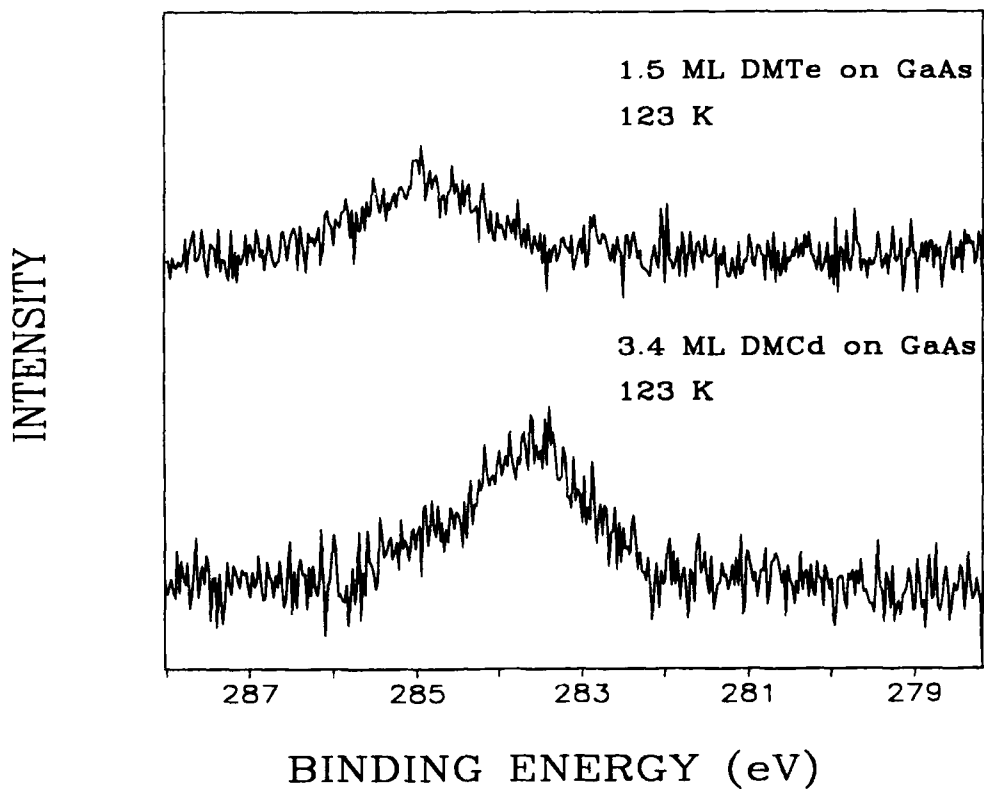


Figure 3.4. C 1s XPS Peaks For a) DMTe And b) DMCd Adsorbed On The GaAs (100) Surface At 123 K.

induced partial decomposition of the physisorbed adspecies and subsequent CH_3 desorption.

Figure 3.5 shows the effect of temperature on the adsorption of DMCd on the GaAs (100) surface. From the uptake data (plots of Cd surface coverage versus DMCd exposure) shown in Figure 3.5(a), it is evident that at 123 K, DMCd continues to adsorb with increasing exposure. For temperatures of 200 K and 300 K, however, the Cd coverage, after an initial rapid increase, saturates at a value on the order of 1.5 to $2 \times 10^{14} \text{ cm}^{-2}$ (i.e. about one monolayer). This is consistent with previously reported room temperature measurements.^{22,23} The reactive sticking coefficient for DMCd on the GaAs (100) surface is obtained directly from the slope of the these curves. At low coverages (i.e., the

initial or clean surface sticking coefficient), this is on the order of 0.1 and is essentially independent of temperature.

Figure 3.5(b) shows Cd $3d_{5/2}$ XPS spectra for substrate temperatures of 123 K, 200 K, 300K and 423 K. These spectra correspond to a Cd surface coverages on the order of $1.5 \times 10^{14} \text{ cm}^{-2}$ which is at or near the saturation coverage for all temperatures except 123 K. For the adspecies formed at 123 K, the Cd $3d_{5/2}$ peak binding energy (consistent with the coverage dependence discussed above) may have a value in the range of 405.1 eV to 405.8 eV depending on the coverage. For temperatures of 200 K, 300K and 423 K, the Cd $3d_{5/2}$ peak binding energy of 405.1 eV is seen to be independent of temperature, and, although not illustrated here, is also essentially independent of surface coverage.

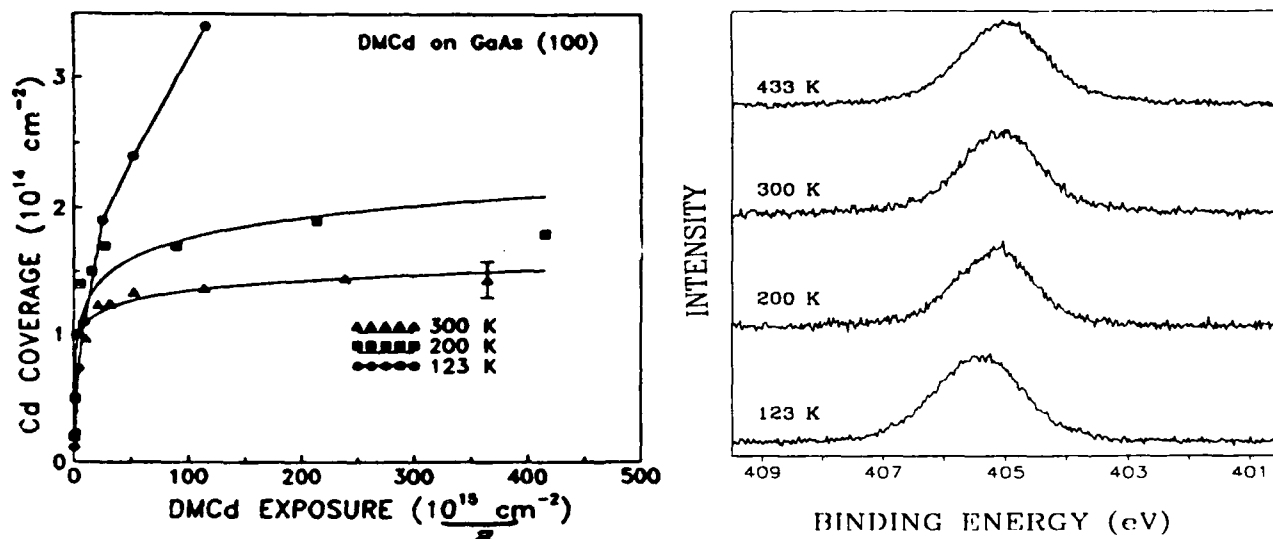


Figure 3.5. a) Cd Surface Coverage Versus DMCd Exposure And b) Cd $3d_{5/2}$ XPS Peaks For Substrate Temperatures Of 300 K, 200 K, and 123 K.

It is believed, as indicated previously, that the adspecies giving rise to the 405.1 eV Cd $3d_{5/2}$ peak is chemisorbed. Relative to the peak for the physisorbed adspecies, the 405.1 eV peak is shifted by 0.7 eV to a lower binding energy, and given the bond strengths for DMCd (56 kcal/mole for the first CH_3 bond),²⁶ it is difficult to believe that the molecule is not at least partially dissociated at 423 K. The observation of a 405.1 eV peak for DMCd adsorbed at 300 K is consistent with previously reported room temperature measurements where monomethyl Cd was suggested as a possible adspecies.^{22,23} This assignment was based on studies which suggest ligand shifts (decreased binding energy relative to the physisorbed adspecies) on the order of 0.5 eV per CH_3 ligand.

Figure 3.6 shows the effects of substrate temperature on the adsorption of DMTe on the GaAs (100) surface. From the plots shown in 3.6(a), DMTe uptake at 123 K and 200 K is very similar, in terms of initial sticking coefficient and saturation levels, to that for DMCd at these temperatures. For temperatures of 300 K and 423 K, the saturation level for DMTe is slightly lower than that for DMCd, and the sticking coefficient appears to fall off somewhat more rapidly with increasing coverage or exposure.

Figure 3.6(b) shows Te $3d_{5/2}$ XPS spectra for substrate temperatures of 123 K, 200 K, 300 K, and 423 K. These spectra correspond to a Te surface coverage on the order of $1 \times 10^{14} \text{ cm}^{-2}$ which is at or near the saturation coverage for 300 K and 423 K. For 123 K and 200 K, the binding energy is 574.9 eV which is characteristic of the physisorbed adspecies. For 300 K and 423 K, respectively, the binding energy is 573.4 eV and 572.5 eV. The value of 572.5 eV agrees quite well with that assigned to Te metal, while the value of 573.4 eV is only 0.3 eV higher than that previously proposed for monomethyl tellurium. Although not illustrated here, these binding energies are essentially independent of surface coverage for each substrate temperature.

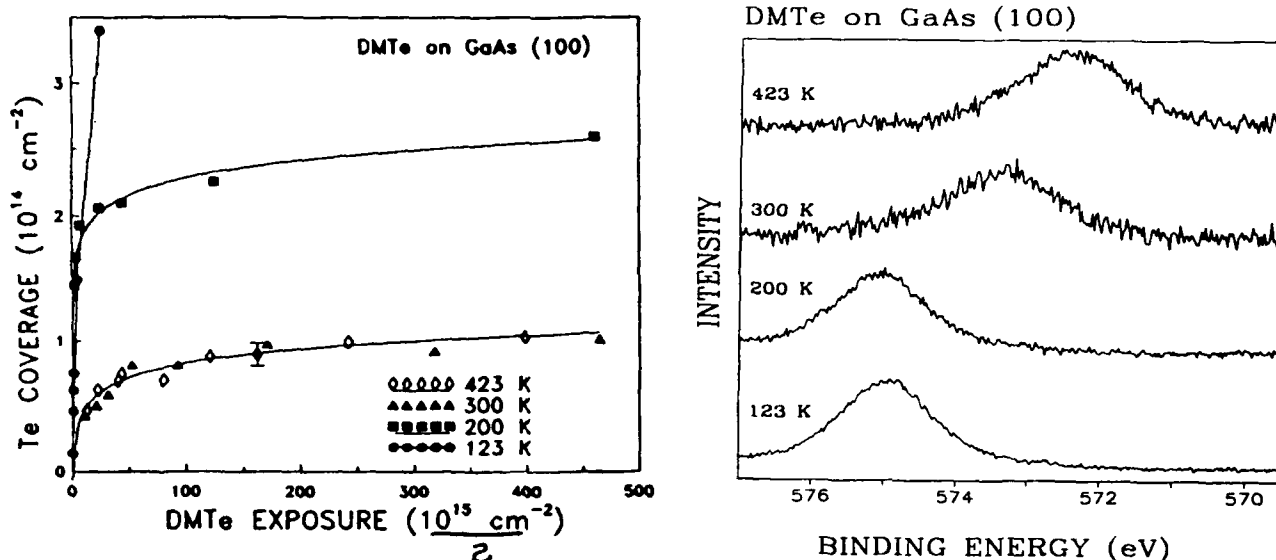


Figure 3.6. a) Te Surface Coverage Versus DMTe Exposure And b) Te $3d_{5/2}$ XPS Peaks For Substrate Temperatures Of 423 K, 300 K, 200 K, And 123 K.

Figure 3.7 shows the Cd and Te $3d_{5/2}$ and the C $1s_{1/2}$ XPS peaks for a 20 nm thick DMCd/DMTe overlayer coadsorbed at 123 K. A comparison of the Cd and Te $3d_{5/2}$ binding energies for these spectra with those for the corresponding monolayer level spectra in Figures 3.1 and 3.2 shows that the overlayer adspecies are physically adsorbed DMCd and DMTe. The increase in the FWHM for the overlayer adspecies (0.4 eV for DMCd and 0.8 eV for DMTe) may be due to either interactions between the coadsorbed molecules or relaxation processes in the photoemission process.

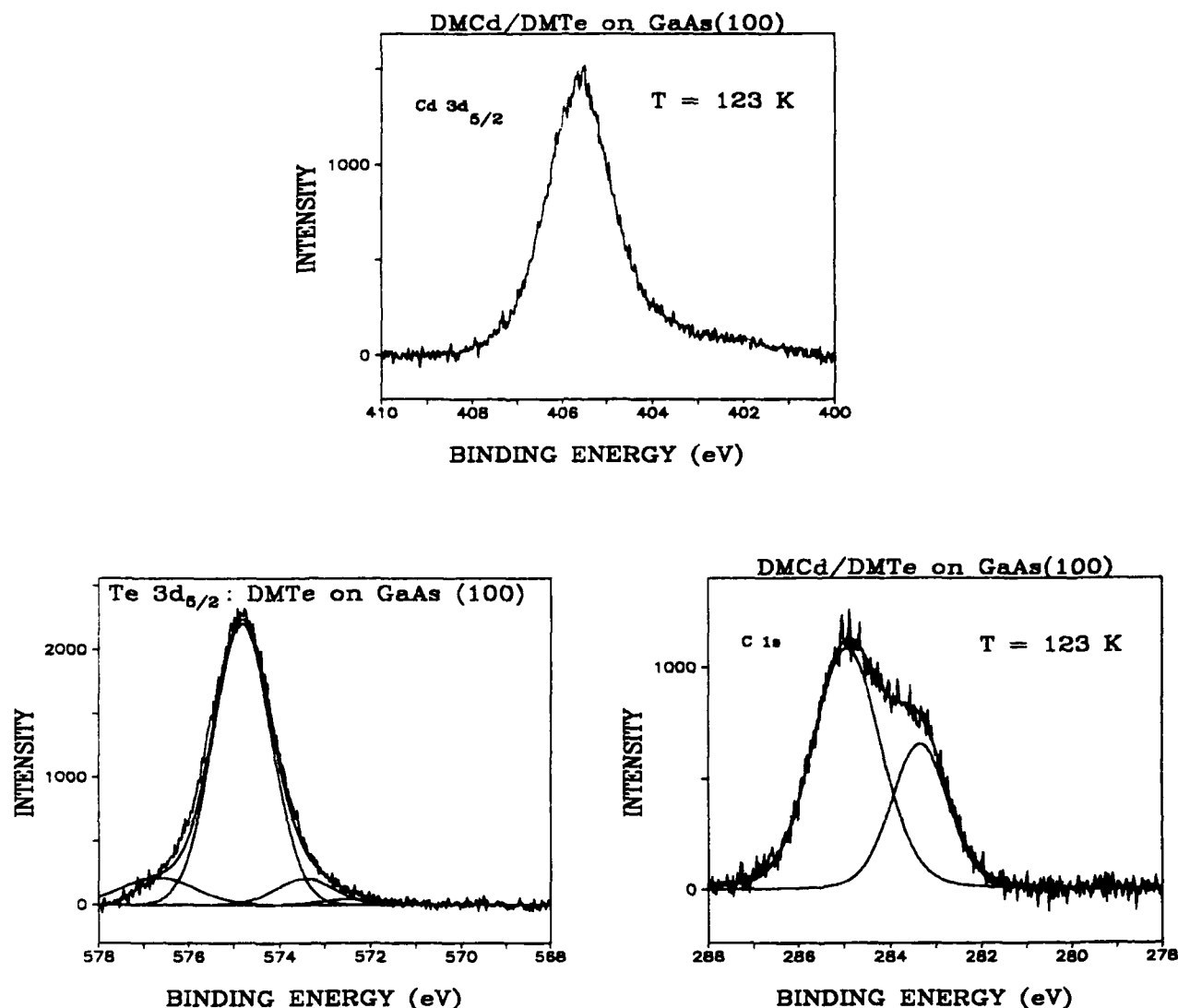


Figure 3.7. a) Cd 3d_{5/2}, b) Te 3d_{5/2}, and c) C 1s_{1/2} XPS peaks for a 20 nm thick DMCd/DMTe overlayer coadsorbed at 123 K.

The C 1s_{1/2} spectrum for the coadsorbed overlayer has been resolved into two underlying peaks located at 283.6 eV and 285.1 eV and having a FWHM of 2.0 eV. These peaks are essentially the same as those previously associated, respectively, with physisorbed DMCd and DMTe. The ratio of the two peak areas indicates a Cd/Te ratio of 0.6 in the overlayer. This agrees within $\pm 15\%$ with the ratio obtained using the Cd and Te 3d_{5/2} peaks and relative sensitivity factors.

3.2 Photon Induced Surface Chemistry and Deposition of CdTe Thin Films

Figures 3.8 to 3.10 show the effects of irradiating a 10 nm thick DMCd/DMTe overlayer, coadsorbed at 123 K, with 193 nm (5 eV) photons at an energy fluence of 6 mJ cm⁻² per pulse. This corresponds to approximately 8×10^{15} photons per cm² per pulse. Figure 3.8 shows the Te 3d_{5/2} XPS peaks as a function of the number of laser pulses. Initially (0 pulses) the peak has a position and shape consistent with the physisorbed DMTe. After 150 pulses, the

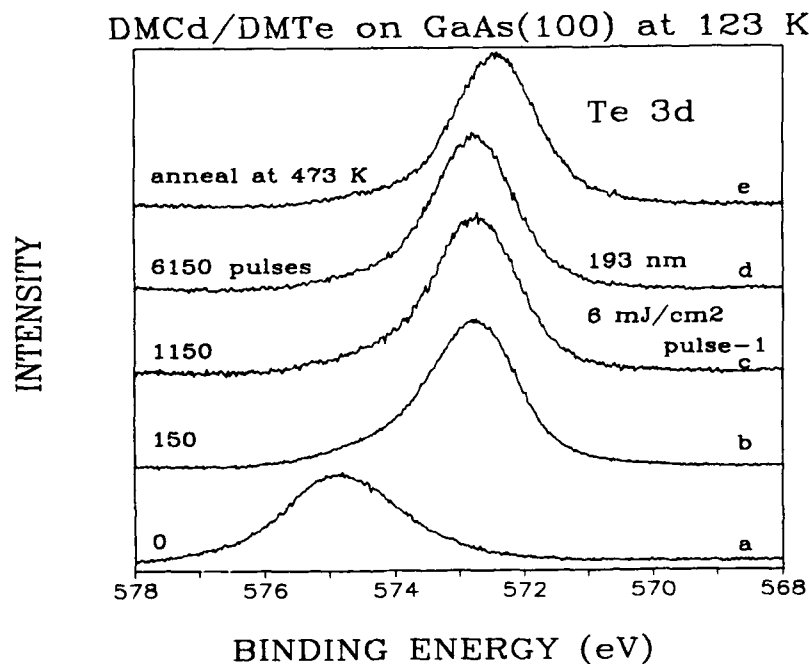


Figure 3.8. Te 3d_{5/2} XPS peaks for a 10 nm thick DMCd/DMTe overlayer coadsorbed at 123 K on the GaAs (100) surface as a function of exposure to 193 nm (5 eV) photons at an energy fluence of 6 mJ cm⁻² per pulse.

The top spectrum shows the results of a subsequent thermal anneal at 473 K. peak has shifted from 574.8 eV to 572.8 eV and the FWHM has decreased from 2.7 eV to 2.0 eV. Increasing the number of pulses to first 1150 and then

6150 has essentially no effect on either the peak position or shape. Annealing the irradiated sample at 473 K for 160 sec moves the peak to a still lower binding energy of 572.4 eV but leaves the FWHM unaltered. This latter binding energy is representative of Te in CdTe. Further, the annealed surface exhibits a 1X1 LEED pattern indicating extensive ordering in the 10 nm thick CdTe overlayer.

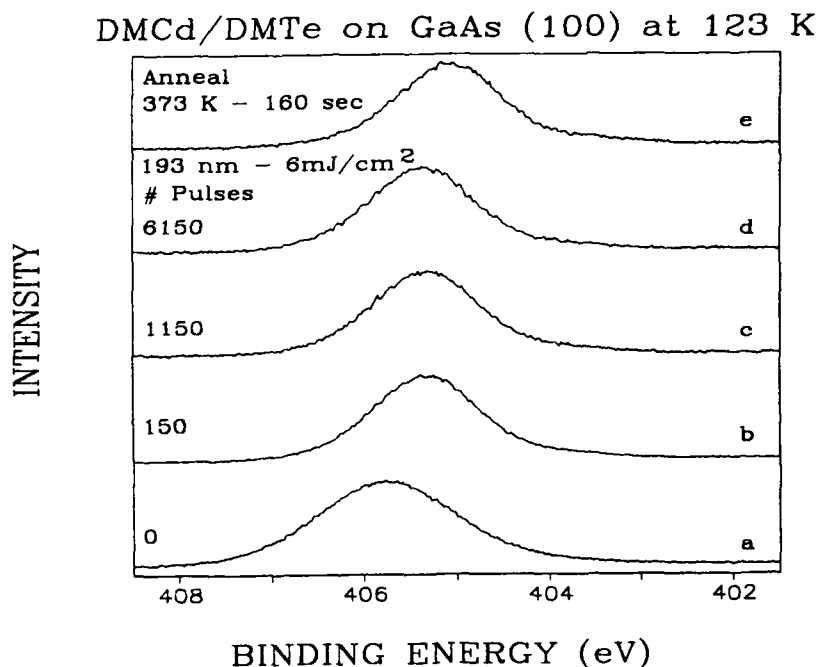


Figure 3.9. Cd 3d_{5/2} XPS peaks for a 10 nm thick DMCd/DMTe overlayer coadsorbed at 123 K on the GaAs (100) surface as a function of exposure to 193 nm (5 eV) photons at an energy fluence of 6 mJ cm⁻² per pulse. The top spectrum shows the results of a subsequent thermal anneal at 473 K.

Figure 3.9 shows the corresponding Cd 3d_{5/2} XPS peaks. The overall effect is similar to but less pronounced than that for Te. Initially (0 pulses) the peak corresponds to the physically adsorbed DMCd. After 150 pulses, the peak shifts from 405.8 eV to 405.4 eV, while the FWHM decreases from 2.3 eV to 1.7 eV. Further irradiation alters neither the peak position nor shape. After

annealing at 473 K for 160 sec, the binding energy decreases to 405.0 eV which is consistent with Cd in CdTe.

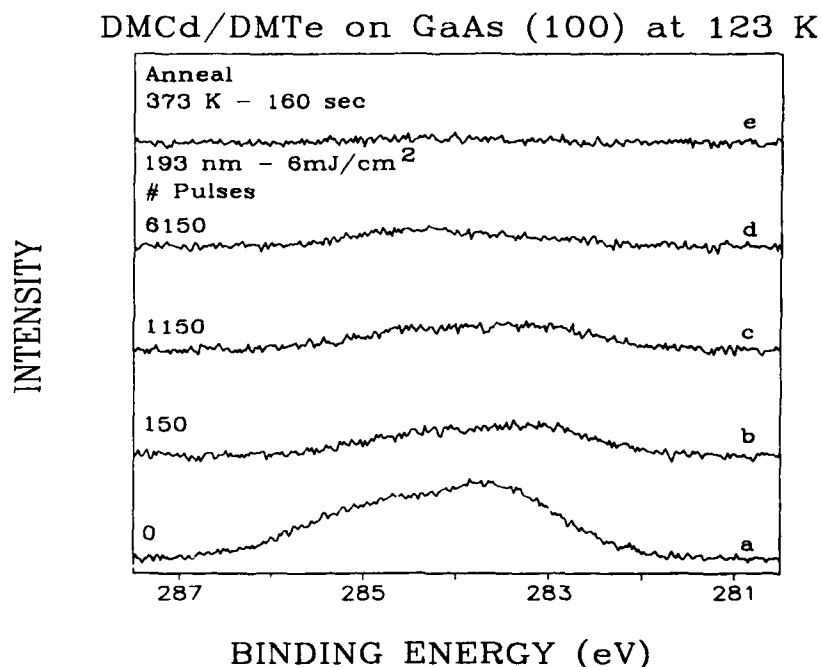


Figure 3.10. C 1s_{1/2} XPS Peaks for a 10 nm thick DMCd/DMTe overlayer coadsorbed at 123 K on the GaAs (100) surface as a function of exposure to 193 nm (5 eV) photons at an energy fluence of 6 mJ cm⁻² per pulse. The top spectrum shows the results of a subsequent thermal anneal at 473 K.

Figure 3.10 shows the corresponding C 1s_{1/2} XPS peaks for the 10 nm thick DMCd/DMTe overlayer. Initially the spectrum consists of two peaks at 283.6 eV and 285.1 eV. These correspond, respectively, to physically adsorbed DMCd and DMTe. After 150 pulses, 50% to 60% of the carbon originally present is removed. Subsequent pulses serve to slowly remove the remaining carbon, and after 6150 pulses 97% of the original carbon has been removed. Annealing the irradiated sample at 473 K for 160 sec reduces the carbon to a level below the XPS detection limit.

The ratio of the two C 1s $\frac{1}{2}$ peaks comprising the initial spectrum indicate the Cd/Te ratio in the overlayer is 1.5. This is in agreement with the value obtained using the Cd and Te 3d $\frac{5}{2}$ peak intensities and relative sensitivity factors. After 150 pulses, the Cd/Te ratio, based the Cd and Te peak intensities, decreases to 0.9 and then remains constant with respect to further irradiation. In general, it was observed that regardless of the stoichiometry of the initial overlayer ($0.5 < \text{Cd/Te} < 2$), the Cd/Te ratio was always unity after irradiation. Annealing the irradiated samples at 473 K for 160 sec had no effect on the one-to-one stoichiometry. However, similar annealing of non-irradiated samples resulted in nearly complete desorption of the overlayer.

An examination of the C 1s $\frac{1}{2}$ spectra before and after irradiation provides additional insight concerning the nature of the photon induced changes in the coadsorbed overlayer. Two representative spectra are shown in Figure 3.11 for a 20 nm thick overlayer. Before irradiation, two peaks corresponding to physisorbed DMCd (283.6 eV) and DMTe (285.1 eV) are observed. After 150 laser pulses of 193 nm radiation at 6 mJ cm $^{-2}$, only one peak at 284.5 eV (FWHM \sim 2.1 eV) is observed. Thus, carbon, originally present in two different chemical environments, is converted by photon induced processes to a single species. Although this species can not be positively identified, the observed binding energy of 284.5 eV is consistent with hydrocarbon production.

Observations for pure irradiated DMCd and DMTe overlayers contrast sharply with those for coadsorbed DMCd/DMTe. For the pure DMTe overlayers, photon irradiation shifts the Te 3d $\frac{5}{2}$ peak to lower binding energy; however, the shift is smaller and requires substantially more laser pulses to achieve. Specifically, the Te 3d $\frac{5}{2}$ peak shifts from 574.8 eV to 573.5 eV (the maximum shift observed for a pure adspecies) after 6000 pulses for pure DMTe; whereas only 150 pulses are required to produce a shift to 572.8 eV for the coadsorbed overlayer. For pure DMCd overlayers, photon irradiation produces essentially no shift in the Cd 3d $\frac{5}{2}$ peak.

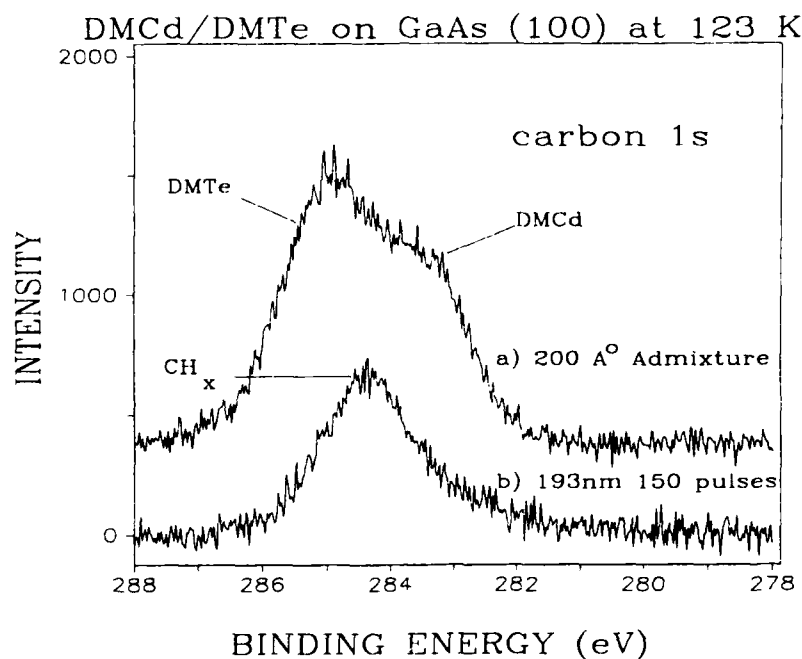


Figure 3.11. C 1s $\frac{1}{2}$ XPS peaks for a 20 nm thick DMCd/DMTe overlayer coadsorbed at 123 K on the GaAs (100) surface a) before and b) after exposure to 193 nm (5 eV) photons at an energy fluence of 6 mJ cm $^{-2}$ per pulse.

These results suggest that laser irradiation initiates a chemical reaction between the coadsorbed metal alkyls in the overlayer with excess metal and carbon species being desorbed. The specific chemical state of the irradiated adspecies can not be determined; however, observation of one-to-one Cd/Te stoichiometry in the irradiated overlayers suggests that at least one bond is formed between Cd and Te. In analogy to gas phase CH $_3$ -Te-Te-CH $_3$, one species which is consistent with this picture is CH $_3$ -Cd-Te-CH $_3$. The anticipated shifts in Cd and Te 3d $\frac{5}{2}$ peaks should be comparable to those observed and the reduction in C 1s $\frac{1}{2}$ peak intensity is comparable to that observed.

Photon initiated reactions between coadsorbed metal alkyls could occur by several different mechanisms. These include: a) chemistry stimulated by hot electrons produced by photons with energies greater than the work function of the substrate (i.e. 193 nm photons have an energy of 5 eV which is greater than the work function for GaAs); b) chemistry induced by thermalization of the photon energy by the substrate; and c) chemistry stimulated by direct absorption of photons by the overlayer. Because hot electrons have mean free paths on the order of 1 nm, they are not likely to be an important factor in stimulating chemistry in thick (10 nm to 20 nm) overlayers. Thus, chemistry stimulated by thermalization or direct photon absorption are the most viable processes.

To determine which of these two mechanisms was responsible, the effects of laser wavelength was investigated. As discussed previously, gas phase DMCd and DMTe undergo single photon dissociation at 193 nm to produce ground state metal atoms, and at this wavelength, large absorption cross sections are anticipated for the coadsorbed species. At 351 nm, however, negligible absorption cross sections are anticipated. Thus, at 351 nm, the extent of the photo-initiated reaction should be reduced if direct absorption is the dominant mechanism. As illustrated in Figure 3.12, this is exactly what is observed.

Figure 3.12 shows the effect of 193 nm and 351 nm photons, at comparable photon and energy fluences, on a DMCd/DMTe overlayer coadsorbed at 123 K. For 193 nm the Te 3d_{5/2} peak has been shifted to 572.8 eV. However, for 351 nm, only broadening of the peak to lower binding energy is observed with the dominant component remaining fixed at 574.9 eV. Whether the broadening is due to thermalization of a small amount of the deposited energy or whether it is due to a larger than anticipated absorption cross section at 351 nm, can not be determined from these data. What is clear, mechanism responsible for the photo-initiated reaction between coadsorbed DMCd and DMTe.

DMCd/DMTe on GaAs (100) at 123 K

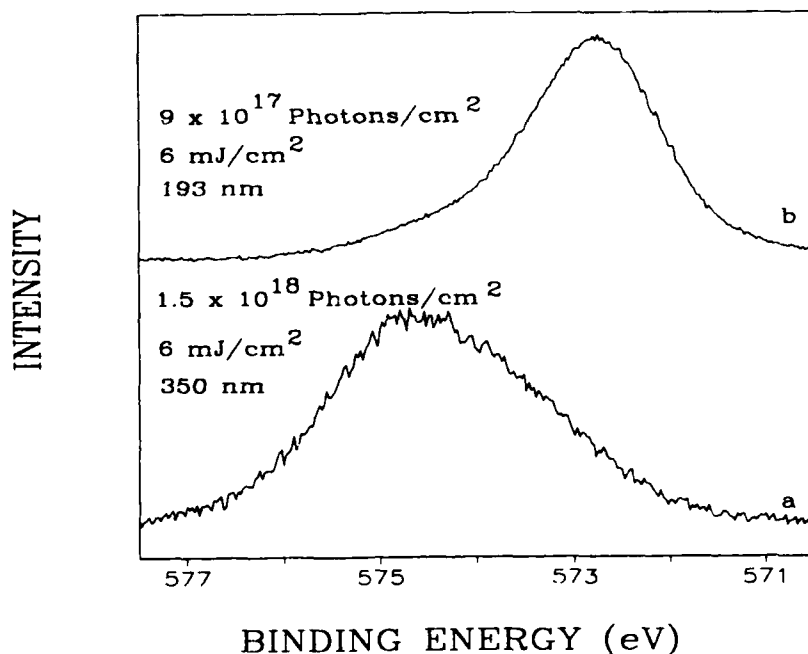


Figure 3.12. XPS spectra of the T3 ed5/2 peak upon irradiation at a) 351 nm and b) 193 nm for equal per pulse fluence and total energy dose.

Whether direct absorption enhances the temperature rise and, thus, induces a thermal reaction in the coadsorbed overlayer, or whether the photo-initiated reaction involves electronically excited species can not be unambiguously determined from these data. Evidence suggesting that thermalization of the directly deposited photon energy plays a relatively minor role is provided by the observation that irradiation at 193 nm produces essentially no change in the pure DMCd overlayer. At this wavelength, the absorption cross section for DMCd is large and thermalization, if it is important, should lead to at least partial decomposition of the DMCd. Instead, no effect is observed, and in fact, it is most likely the rapid channeling of energy out of the excited DMCd molecules (in the absence of excited DMTe) and into the substrate (i.e. thermalization) which prevents partial decomposition of the irradiated DMCd overlayer. The limited extent of the photo-initiated

decomposition of pure DMTe may also be due to thermalization of energy deposited in the molecule in the absence of DMCd.

4 CONCLUSIONS

An epitaxial thin film (~ 100 Å) of CdTe on GaAs (100) has been produced by 193 nm photon irradiation of beam deposited admixtures of dimethyl tellurium and cadmium at substrate temperatures of 123 K followed by a thermal anneal at 473 K. The resultant LEED pattern is 1×1 indicating an epitaxial (100) CdTe surface. The process is quite efficient at a laser fluence of 6 mJ cm^{-2} . The initial stoichiometric Cd-Te deposit produced by the laser irradiation is the result of a photon initiated reaction between the adsorbed metal organic adspecies. The carbon content of this reaction product is about half of the original overlayer. The annealing step reduces carbon levels below the XPS detection limit ($\sim 0.5\%$).

The advantages of making II-VI compound semiconductors by this technique are apparent. By using a cold GaAs (123 K) substrate, we have increased sticking coefficients to 0.1 - 0.3, two to three orders of magnitude greater than that found at typical growth temperatures (500-600 K), thus saving on usage of metal alkyl precursors. Another potential advantage is the photo-induced "fixing" of the chemical reaction to produce CdTe. The fact that desorption occurs in non-irradiated areas suggests that LSCE may be used for patterned deposition. A drawback at this point is the need to anneal the sample of 473 K to remove the carbon contamination and product epitaxial ordering. But, if pulsed laser annealing could be utilized, this problem could be overcome. Future work is indicated in the area of ternary compounds, such as HgCdTe. Dimethyl mercury also absorbs strongly at 193 nm and thus is a candidate for laser surface chemical epitaxy. Thus, the potential for fabricating HgTe/CdTe quantum well structures, where limited interdiffusion is required, is indicated.

5 REFERENCES

1. A. O'Neill, P. Shaw, E. Sanchez, Z. Wu, and R.M. Osgood, Jr., "Surface Spectroscopic Studies of Organometallic Deposition," Mat. Res. Soc. Symp. **129**, (1989).
2. J.J. Zinck, P.D. Brewer, J.E. Jensen, G.L. Olsen, and L.W. Tuh, Appl. Phys. Lett. **52**, 1434 (1988); J.B. Mullin and S.J.C. Irvine, J. Vac. Sci. Technol. **A4**, 700 (1986).
3. E. Tokumitsu, Y. Kurow, M. Kanogai, and K. Takahashi, J. Appl. Phys. **55**, 3163 (1984).
4. C. D. Stinespring and A. Freedman, "Laser-Induced Surface Chemical Epitaxy of CdTe on GaAs (100)", Mat. Res. Soc. Symp. Proc.
5. C. D. Stinespring and A. Freedman, "Laser-Induced Surface Chemical Epitaxy", SPIE Symp. Proc. on Microelectronic Integrated Processing (in press).
6. R.A. Wood and R.J. Hager, J. Vac. Sci. Technol. **A1**, 1608 (1983).
7. C. Jonah, P. Chandra, and R. Bersohn, J. Chem. Phys. **55**, 1903 (1971), C.F. Yu, F. Youngs, K. Tsukiyama, R. Bersohn, and J. Preses, J. Chem. Phys. **85**, 1382 (1986).
8. C.J. Chen and R.M. Osgood, J. Chem. Phys. **81**, 327 (1984).
9. P.D. Brewer, J.E. Jensen, G.L. Olsen, L.W. Tutt, and J.J. Zinck, Proc. Mat. Res. Soc. Symp. **101**, 327 (1988); P.D. Brewer, Chem. Phys. Lett. **141**, 301 (1987).
10. V.M. Donnelly, J.A. McCaulley, V.R. McCrary, C.W. Tu, and J.C. Beggy, "Selective Area Growth of GaAs by Laser Induced Pyrolysis of Absorbed Gallium-Alkyls," Proc. Mat. Res. Soc. Symp., **129** (1989).
11. D. Burgess, P.C. Stair, and E. Weitz, J. Vac. Sci. Technol. **A4**, 1362 (1986); P.C. Stair and E. Weitz, J. Opt. Soc. Am. **B4**, 255 (1987).
12. L.A. Kolodziejcki, R.L. Gunshor, N. Otsuka, S. Datta, W.M. Becker, and A.V. Nurmikko, IEEE J. Quantum Electron. **QE-22**, 1666 (1986).
13. T.A. Carlson, "Photoelectron and Auger Spectroscopy," Plenum Press, New York (1978).

14. C.D. Wagner in "Handbook of X-Ray and Ultra-Violet Photoelectron Spectroscopy," ed. by D. Briggs, Heydon and Sons, London (1977).
15. S.W. Gaarenstroom and N. Winograd, J. Chem. Phys. **67**, 3500 (1977).
16. "Handbook of X-Ray Photoelectronic Spectroscopy," ed. by G.E. Muilenberg, Perkin-Elmer Corp., Eden Prairie, MN (1979).
17. M.K. Bahl, R.L. Watson, and K.J. Irgolic, J. Chem. Phys. **66**, 5526 (1977).
18. M.K. Bahl, R.L. Watson, and K.J. Irgolic, J. Chem. Phys. **68**, 3272 (1978).
19. M.K. Bahl, R.D. Woodall, R.L. Watson, K.J. Irgolic, J. Chem. Phys. **64**, 1210 (1976).
20. K. Siegbahn, C. Nording, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, Electron Spectroscopy for Chemical Analysis - Atomic, Molecular, and Solid State Structure Studies by Means of Electron Spectroscopy (Almqvist and Wiksells Boktryckeri AB, Stockholm, Sweden, 1967); Nova Acta Regiae Soc. Sci., Upsalienis, Ser. IV 20, (1967).
21. U. Gelius, P.F. Heden, J. Hedman, B.J. Lindberg, R. Manne, R. Nordberg, C. Nording, and K. Siegbahn, Physica Scripta **2**, 70 (1970).
22. C.D. Stinespring and A. Freedman, Chem. Phys. Lett. **143**, 584 (1988).
23. C.D. Stinespring and A. Freedman, Appl. Phys. Lett. **52**, 1959 (1988).
24. T.E. Mady, J.T. Yates, and N.E. Erickson, Chem. Phys. Lett. **19**, 487 (1973).
25. E.P. Marsh, T.L. Gilton, W. Meiler, M.R. Schneider, and J.P. Cowin, Phys. Rev. Lett. **61**, 2535 (1988); T.L. Gilton, C.P. Dehnbostel, and J.P. Cowin, J. Chem. Phys. **91**, 1937 (1989).
26. J. Ibuki, A. Hiraya, and K. Shobatake, J. Chem. Phys. **92**, 2797 (1990).

6. PROGRAM MANAGEMENT

6.1 Key Personnel

DR. ANDREW FREEDMAN

EDUCATION

Ph.D. (Physical Chemistry) University of California, Berkeley, 1977
B.S. (Chemistry) Yale College, 1971

EXPERIENCE

Dr. Freedman joined the Research Group of Aerodyne Research, Inc. in July 1979 as a Senior Research Scientist and has since been promoted to Principal Research Scientist. He also currently serves as Manager of Laboratory Operations and as Associate Director of the Center for Chemical and Environmental Physics. At this time, Dr. Freedman is heavily involved in the area of materials modification. His work in plasma etching of electronic materials (funded by the National Science Foundation) includes measuring key gas phase reaction rates involving silicon free radical species and a study of gas-surface interactions of atomic fluorine with silicon using molecular beam techniques. He has extended this work to include chlorine atom reactions with gallium arsenide with the goal of achieving controlled etching of very thin films. An outgrowth of this work has been a project (funded by the Office of Naval Research) to fluorinate diamond thin films to create surfaces with reduced friction and increased wear resistance. The goal of this project is to develop a commercially viable process for coating bearings, seals, and other sliding surfaces which need to operate under harsh conditions.

Dr. Freedman is also involved in the area of II-VI electronic materials deposition. In a project funded by the Air Force Office of Scientific Research, he has developed a technique, laser surface chemical epitaxy, which has produced epitaxial thin films of cadmium telluride on gallium arsenide substrates. This clean, low temperature deposition technique utilizes the efficiency of excimer lasers in photolytically decomposing adsorbed metal organic species which subsequently react to form a compound semiconductor. This technique, applicable to mercury cadmium telluride and other II-VI compounds, offers the possibility of in-situ patterned deposition.

A major portion of Dr. Freedman's time has been spent developing a high velocity, high flux molecular beam source of atomic oxygen. In conjunction with the Air Force Geophysics Laboratory, he has used this source to study vibrational excitation mechanisms in carbon dioxide and water molecules. An outgrowth of this work has been a project to study spacecraft luminescence caused by surface-gas interactions.

Another interest of Dr. Freedman has been the problem of in-situ monitoring of atmospheric gases. He was program manager of a National Science Foundation (NSF) sponsored project to measure atmospheric fluxes of methane, a contributor to the so-called "greenhouse effect". Methane fluxes are measured using a sonic anemometer to determine wind velocities while detecting methane concentration fluctuations using absorption of the Helium-Neon laser line at 3.39 μm which is coincident with a methane absorption feature. He has also been funded by both NSF and the Electric Power Research Institute to develop spectroscopic techniques for detection of large organic molecules such as chlorinated aromatic hydrocarbons. Dr. Freedman devised a detection scheme based on photofragment spectroscopy which utilizes the large ultraviolet absorption cross sections of aromatic molecules.

Dr. Freedman has also been involved in determining the role of phosphorus species in coal-fired open cycle magnetohydrodynamic (MHD) power generation. He has helped in identifying the key phosphorus species (both charged and neutral) which affect generator efficiency by the use of molecular beam sampling mass spectrometry and has determined the thermochemistry of these species by direct conductivity measurements utilizing a high temperature laboratory-scale combustor.

Before joining Aerodyne, Dr. Freedman was a post-doctoral research associate in the Chemistry Department of Columbia University where he studied energy partitioning in the process of photodissociation of polyatomic molecules in the gas phase. The fragments produced by the single photon UV laser induced photodissociation were interrogated using molecular beam time-of-flight techniques and laser induced fluorescence. Dr. Freedman's thesis work involved use of crossed molecular beams to study the reactive scattering of high temperature atomic and molecular species with various reagents.

CHARTER D. STINESPRING

EDUCATION

Ph.D. (Physics) West Virginia University, 1975

M.S. (Physics) West Virginia University, 1972

B.S. (Physics and Mathematics) Salem College, 1969

EXPERIENCE

Dr. Stinespring joined Aerodyne Research, Inc. in June 1981 as a Senior Research Scientist and in 1984 was promoted to Principal Research Scientist. His work has focused on fundamental and applied topics in surface and materials science including studies of gas surface reactions, surface segregation, and gas phase diffusion and reaction kinetics. A major thrust of this work has been to develop or improve a number of electronic materials growth and processing techniques. Specific examples include studies of

fluorine atom-silicon surface reactions related to plasma etching, studies of photon-adspecies interactions associated with photo-induced epitaxy of II-VI and III-V compounds, and studies of surface reactions associated with silicon carbide epitaxy. These studies have utilized surface analytical techniques as in situ diagnostics under ultrahigh vacuum conditions. In addition, theoretical models have been developed for describing surface segregation and chemical vapor deposition. Dr. Stinespring's research has been supported by DOE, NASA, NSF, AFOSR, industrial, and university funds.

Before joining Aerodyne, Dr. Stinespring was a Research Physicist in the Exploratory Research Branch at the Department of Energy's Morgantown Energy Technology Center for six years. In this position, he was responsible for the research activities of the Center's Surface Science Laboratory. These included studies of surface segregation, evaporation, and adsorption of alkali atoms and alkali containing molecules related to alkali control in combustion systems, studies of SO₂ adsorption on alkaline earth oxides for controlling sulfur emissions, and studies of aluminosilicate particle transformations in combustion systems. Experimental techniques used in these studies include XPS, UPS, SIMS, AES, SAM, TGA, DTA, XRF, and XRD.

Dr. Stinespring was an NDEA fellow and an Instructor of Physics during his graduate studies at West Virginia University. His M.S. and Ph.D. research in solid state physics involved experimental and theoretical analyses of magnetoelastic interactions in ferromagnetic materials. Quantum and classical field theoretical calculations were performed to predict the magnetic field dependence of the materials elastic constants and ultrasonic pulse-echo measurements were performed to verify the calculations.

6.2 Presentations

"Laser Induced Surface Chemical Epitaxy," International Laser Science Conference, Seattle WA (June 1986)

"Laser Induced Surface Chemical Epitaxy," National Meeting, American Physical Society, New York (March 1987)

"Thermal and Photon Induced Chemistry of Adsorbed Cadmium and Tellurium Alkyls", Materials Research Society Conference, Boston, MA (November 1987)

"Thermal and Photolytic Decomposition of Adsorbed Cadmium and Tellurium Alkyls", Materials Research Society Conference, Boston, MA (November 1988)

"Laser-Induced Surface Chemical Epitaxy of CdTe on GaAs (100)," American Vacuum Society, Boston MA (October 1989)

"Laser-Induced Surface Chemical Epitaxy", C. D. Stinespring and A. Freedman, SPIE Symposium on Integrated Processing, Santa Clara, CA (October 1989)

"Laser-Induced Surface Chemical Epitaxy," AFOSR Surface Chemistry Program Review, Captiva Island, FL (October 1989)

Laser-Induced Surface Chemical Epitaxy of CdTe on GaAs (100)", Materials Research Society Conference, Boston, MA (November 1989)

6.3 Publications

"Thermal and Photon Induced Chemistry of Adsorbed Cadmium and Tellurium Alkyls", C. D. Stinespring and A. Freedman, Mat. Res. Soc. Symp. Proc. 101 (1988) 331.

"Photolytic Decomposition of Adsorbed Cadmium and Tellurium Alkyl Species at 295 K Upon 193 nm Photon Irradiation", C. D. Stinespring and A. Freedman, Appl. Phys. Lett. 52 (1988) 1959.

"Thermal Surface Chemistry of Dimethyl Cadmium and Dimethyl Tellurium at 195 K", C. D. Stinespring and A. Freedman, Chem. Phys. Lett. 143 (1988) 548.

"Thermal and Photolytic Decomposition of Adsorbed Cadmium and Tellurium Alkyls", C. D. Stinespring and A. Freedman, Mat. Res. Soc. Symp. Proc. 129, 57 (1989),

"Laser-Induced Surface Chemical Epitaxy of CdTe on GaAs (100)", C. D. Stinespring and A. Freedman, Mat. Res. Soc. Symp. Proc. (in press).

"Laser-Induced Surface Chemical Epitaxy", C. D. Stinespring and A. Freedman, SPIE Symp. Proc. on Microelectronic Integrated Processing (in press).

"Thermal and Photon-Induced Surface Interactions of Dimethyl Cadmium and Dimethyl Tellurium on GaAs (100)", C. D. Stinespring and A. Freedman, To be submitted to J. Phys. Chem.

"Laser-Induced Surface Chemical Epitaxy of CdTe on GaAs (100)", C. D. Stinespring and A. Freedman, J. Appl. Phys. (To be submitted to Appl. Phys. Lett.)

Photolytic decomposition of adsorbed tellurium and cadmium alkyl species at 295 K upon 193 nm photon irradiation

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The photolytic decomposition of adspecies formed by the adsorption of tellurium and cadmium alkyls at 295 K under ultrahigh-vacuum conditions has been studied using x-ray photoelectron spectroscopy. Dimethyl tellurium adsorbed at submonolayer coverages on a polycrystalline gold substrate has been observed to undergo nearly quantitative photolytic decomposition at 193 nm to form metallic tellurium. The hydrocarbon photofragments produced in the decomposition lead to negligible carbon contamination on the gold surface. Dimethyl cadmium adsorbed on amorphous SiO_2 both desorbs and decomposes to form the metal adspecies. In this case, most of the carbon remains as hydrocarbon and carbidic contaminants. Monomethyl adspecies of both metals formed on $\text{Si}(100)$ and $\text{GaAs}(100)$ surfaces are inactive with respect to decomposition at the low fluences (0.25 mJ cm^{-2}) used in these experiments; however, substantial desorption is observed.

Photolytic decomposition of adsorbed organometallic compounds under high-vacuum conditions offers the potential of controlled epitaxial growth of compound semiconductor thin films.¹ This realization has spurred research in this area over the last two years; adsorbed molecules studied so far include alkyl halides,²⁻⁵ metal carbonyls,⁶⁻⁹ and III-V metal alkyls.¹⁰⁻¹² We present an initial study of the II-VI metal alkyl compounds dimethyl tellurium and cadmium. These two compounds represent comparatively simple molecules in that they have only two organic ligands compared to three for III-V organometallics and four to six or more for metal carbonyls. Furthermore, the gas phase photochemistry of dimethyl cadmium in the 193 nm region has been previously studied. It is known to have a large photoabsorption cross section and to decompose on a subpicosecond time scale to form cadmium atoms and two methyl radicals.¹³⁻¹⁶ Thus one might expect molecularly chemisorbed or physisorbed dimethyl cadmium to decompose on a surface upon 193 nm photon irradiation if energy transfer to the surface via adspecies-surface interactions is comparatively slow. Recent work on dimethyl tellurium suggests similar behavior.¹⁷

Details of our experimental procedure are given elsewhere.¹⁸ Briefly, substrate samples were exposed to a known dose of metal alkyl gas using backfilling techniques in an ultrahigh-vacuum reaction chamber (base pressure $\approx 3 \times 10^{-9}$ Torr) and transferred *in vacuo* into an analysis chamber where x-ray photoelectron spectroscopy (XPS) was used to monitor adspecies coverage and chemical state. The sample was then returned to the reaction chamber where it was irradiated with light pulses at 193 nm produced by an ArF excimer laser (Questek). After irradiation, the sample was again analyzed using XPS to determine the photochemistry induced by the laser pulses. The XPS analyses were performed using a PHI 15 kV, Mg $K\alpha$ x-ray source and a PHI double-pass cylindrical-mirror electron energy analyzer operated at a pass energy of 50 eV. The analyzer was calibrated using the Au $4f_{7/2}$ photoelectron peak at 83.8 eV. For the SiO_2 surface, sample charging effects were taken

into account by referencing the spectra to the Si $2p$ photoelectron peak at 103.4 eV.

Substrates studied included single-crystal $\text{GaAs}(100)$ and $\text{Si}(100)$ as well as polycrystalline Au and amorphous SiO_2 . All substrates were cleaned by Ar^+ ion etching (1 keV), and the crystalline $\text{GaAs}(100)$ and $\text{Si}(100)$ samples were annealed at 850 and 1100 K, respectively, to restore surface order. Dimethyl cadmium and tellurium (Alfa) were used as supplied without further purification. Based on XPS survey spectra, no evidence of contaminant species from either these gases or reaction with residual gases in the vacuum chamber was observed. The laser fluence was controlled using a simple two-element beam expander which provided a low divergence beam (1 cm diameter) which entered the reaction chamber through a Suprasil window. Laser fluences were kept at 0.25 mJ cm^{-2} to minimize the effect of surface heating ($< 3 \text{ K}$).¹⁹ All experiments were performed with the substrate at 295 K.

As described in Ref. 18, XPS analyses of the Cd and Te $3d_{5/2}$ peaks for adspecies on the various substrates led to the identification of three distinct binding energies for each peak. Within the experimental uncertainty of $\pm 0.2 \text{ eV}$, the peaks observed at 404.6 and 572.6 eV correspond well with cadmium²⁰ and tellurium²¹ metal. The remaining peaks (405.1 and 405.6 eV for cadmium and 373.1 and 573.6 eV for tellurium) correspond well with monomethyl and dimethyl species, respectively. These assignments are in agreement with studies of tellurium compounds (solids at 295 K) by Bahl *et al.*,²¹ and electronegativity and ligand shift arguments for the analogous cadmium compounds,^{22,23} which indicate shifts of $+0.5 \text{ eV}$ per CH_3 ligand. Based on these considerations, the thermal surface chemistry of dimethyl cadmium and tellurium on the four substrates may be summarized as follows. Dimethyl cadmium dissociatively chemisorbs to form metal adspecies on Au and monomethyl adspecies on GaAs and Si , while molecularly chemisorbed or physisorbed adspecies are formed on SiO_2 . Dimethyl tellurium dissociatively chemisorbs to form monomethyl and

TABLE I. Photoeffect of 193 nm irradiation.

Adspecies	Effect	Substrate
(CH ₃) ₂ Te	Conversion to Te	Au
(CH ₃) ₂ Cd	Conversion to Cd and partial desorption	SiO ₂
(CH ₃) Te	Partial desorption	GaAs
(CH ₃) Cd	Partial desorption	GaAs
		Si
Te	None	Au, GaAs
Cd	None	Au, SiO ₂

metal adspecies on GaAs, while metal and molecularly chemisorbed adspecies are formed on Au. For Si and SiO₂ surfaces, the dimethyl tellurium sticking coefficient was sufficiently low that no adspecies are observed using XPS.

Table I summarizes the effects of 193 nm laser irradiation on each adspecies formed by the thermal surface chemistry. At the low laser fluences and total doses used in these experiments, no effect was found for either metal adspecies. For the monomethyl adspecies, no conversion to the metal was observed, although some desorption ($\approx 50\%$) of the monomethyl species occurred. Physisorbed or molecularly chemisorbed dimethyl tellurium and cadmium were converted directly to the metal adspecies without the appearance of monomethyl species. This result is illustrated in Figs. 1 and 2.

The lower spectrum in Fig. 1 shows the Te 3d_{5/2} XPS peak for Au exposed to dimethyl tellurium at 295 K to pro-

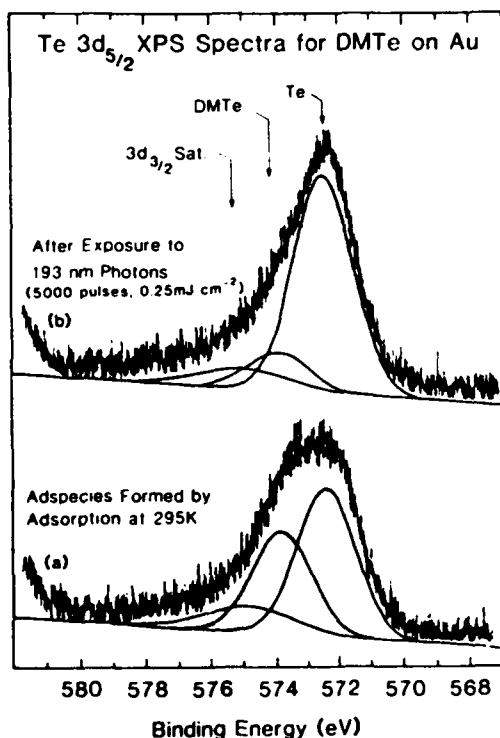


FIG. 1. Te 3d_{5/2} XPS spectrum for dimethyl tellurium adspecies on Au (a) before and (b) after irradiation by 5000 pulses of 193 nm laser light at 0.25 mJ cm⁻² per pulse. These spectra have been resolved into metal (572.6 eV) and dimethyl tellurium (573.6 eV) components. The low level peak at 574.8 eV is an x-ray satellite associated with the Te 3d_{3/2} peak.

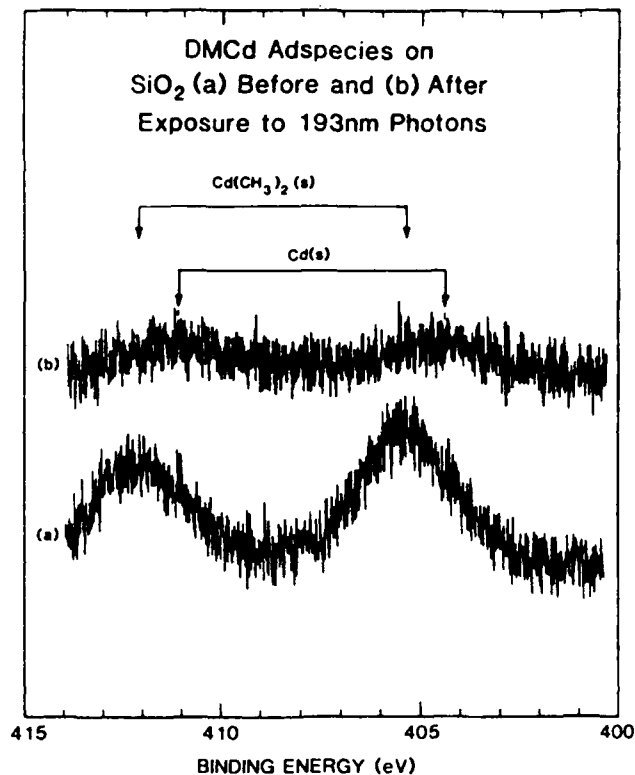


FIG. 2. Cd 3d XPS spectra for dimethyl cadmium adspecies on SiO₂ (a) before and (b) after irradiation by 5000 pulses of 193 nm laser light at 0.25 mJ cm⁻² per pulse.

duce a tellurium adspecies coverage¹⁸ of $\approx 4 \times 10^{14}$ cm⁻². The thermal chemistry produces both tellurium and dimethyl tellurium adspecies. The upper spectrum shows the effect of irradiating these adspecies by 193 nm photons at 0.25 mJ cm⁻² for 5000 pulses. The decrease in intensity of the physisorbed or molecularly chemisorbed dimethyl tellurium peak and the corresponding increase in intensity of the metal peak indicate essentially quantitative conversion of the dimethyl tellurium to tellurium adspecies with no measurable desorption of the original adspecies. It is interesting to note that further irradiation of the sample by an additional 5000 pulses does not eliminate this residual ($\approx 15\%$) dimethyl tellurium adspecies. The C 1s peak (hydrocarbon in nature) observed after irradiation is consistent with the residual dimethyl tellurium adspecies coverage. This indicates that the methyl groups produced from the decomposition process desorb from the surface. Assuming that the adspecies photoabsorption cross section is similar to that found in the gas phase¹⁷ (≈ 0.2 Å²), the conversion to metallic tellurium appears to be an efficient process which provides evidence for a single-photon interaction.

The lower spectrum in Fig. 2 shows the Cd 3d peaks for Au exposed to dimethyl cadmium at 295 K to produce a cadmium adspecies coverage¹⁸ of $\approx 2 \times 10^{13}$ cm⁻², and the upper spectrum shows the effect of irradiating these adspecies with 193 nm photons at 0.25 mJ cm⁻² for 5000 pulses. As can be seen by the relative intensities of the XPS peaks before and after irradiation, approximately 80% of the dimethyl cadmium species is desorbed, and almost all of the

remaining cadmium species have been converted to the metallic state. Given the observed low adspecies coverages, however, an alternate channel in which the metal adspecies are simply revealed by the photodesorption of overlying molecularly chemisorbed adspecies cannot be ruled out based on these results alone. The observation of desorption, in either case, is consistent with a simple model presented in Ref. 18. This model predicts that the interaction of SiO_2 with dimethyl cadmium should be relatively weak because of the insulating nature of SiO_2 and consequent unavailability of electronic charge for back bonding to the vacant p orbitals on the cadmium atom. These same arguments also argue against the formation of cadmium metal adspecies on SiO_2 via dissociative chemisorption processes.

In contrast to the case of irradiated dimethyl tellurium on Au, the C 1s XPS peak intensity for dimethyl tellurium on SiO_2 is the same before and after laser irradiation. Furthermore, after irradiation, the C 1s peak has a carbidic as well as a hydrocarbon component, which indicates that methyl groups produced by the photodissociation process strongly interact with the surface.

In conclusion, we have observed the semiquantitative photolytic conversion (with 193 nm photons) of physisorbed or molecularly chemisorbed dimethyl tellurium adspecies on a Au substrate to form metallic tellurium at 295 K. For physisorbed or molecularly chemisorbed dimethyl cadmium on SiO_2 , desorption is the major channel, with approximately 20% of the dimethyl cadmium adspecies being converted to metallic cadmium. Irradiation of dissociatively chemisorbed monomethyl adspecies of both tellurium and cadmium on GaAs(100) and Si(100) leads to partial desorption, but not to decomposition. Once metallic species are produced on all surfaces, they appear to be impervious to irradiation at the low fluences used in these experiments.

Motivated by the potential for controlled epitaxial growth of compound semiconductor thin films, future studies will seek a more fundamental understanding of the thermal and photon-induced chemistry of organometallic adspecies. Of particular interest in this regard are the effects of key parameters such as laser wavelength as well as surface temperature, orientation, and structure, and the role of the ligand groups. To grow epitaxial layers of compound semiconductors, for instance, reduced temperatures may favorably alter the thermal reaction product distribution by increasing the amount of adsorbed dimethyl adspecies at the expense of photolytically inactive monomethyl adspecies. An alternative approach, based on the observation that gas

phase monomethyl cadmium and tellurium absorb in the 260–285 and 225–245 nm region, respectively,²⁴ is to use different laser wavelengths. In any case, an understanding of these and other aspects of the thermal and photon-induced surface chemical deposition techniques must be understood for controlled epitaxial growth of electronic materials.

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- ¹J. Nishizawa, Y. Kokubun, H. Shimawaki, and M. Koike, *J. Electrochem. Soc.* **132**, 1939 (1985); J. Nishizawa, H. Abe, T. Kurabayashi, and N. Sakurai, *J. Vac. Sci. Technol. A* **4**, 706 (1986); J. Nishizawa, K. T. Kurabayashi, H. Abe, and N. Sakurai, *J. Vac. Sci. Technol. A* **5**, 1572 (1987).
- ²E. B. D. Bourdon, J. P. Cowin, I. Harrison, J. C. Polanyi, J. Segner, C. D. Stanners, and P. A. Young, *J. Phys. Chem.* **88**, 6100 (1984).
- ³F. L. Tabares, E. P. Marsh, G. A. Bach, and J. P. Cowin, *J. Chem. Phys.* **86**, 738 (1987).
- ⁴E. P. Marsh, F. L. Tabares, M. R. Schneider, and J. P. Cowin, *J. Vac. Sci. Technol. A* **5**, 519 (1987).
- ⁵T. J. Chuang and K. Domen, *J. Vac. Sci. Technol. A* **5**, 473 (1987).
- ⁶J. R. Creighton, *J. Appl. Phys.* **59**, 410 (1986).
- ⁷N. S. Gluck, Z. Ying, C. E. Bartosch, and W. Ho, *J. Chem. Phys.* **86**, 4957 (1987).
- ⁸F. G. Celii, P. M. Whitmore, and K. C. Janda, *Chem. Phys. Lett.* **138**, 257 (1987).
- ⁹J. R. Swanson, C. M. Friend, and Y. J. Chabal, *J. Chem. Phys.* **87**, 5028 (1987).
- ¹⁰G. S. Higashi and L. J. Rothberg, *Appl. Phys. Lett.* **47**, 1288 (1985).
- ¹¹G. S. Higashi, L. J. Rothberg, and G. C. Fleming, *Chem. Phys. Lett.* **115**, 167 (1985).
- ¹²D. J. Ehrlich and R. M. Osgood, Jr., *Chem. Phys. Lett.* **79**, 381 (1981).
- ¹³C. Jonah, P. Chandra, and R. Bersohn, *J. Chem. Phys.* **55**, 1903 (1971).
- ¹⁴C. F. Yu, F. Youngs, K. Tsukiyama, R. Bersohn, and J. Preses, *J. Chem. Phys.* **85**, 1382 (1986).
- ¹⁵C. J. Chen and R. M. Osgood, *J. Chem. Phys.* **81**, 327 (1984).
- ¹⁶J. O. Chu, G. W. Flynn, C. J. Chen, and R. M. Osgood, *Chem. Phys. Lett.* **119**, 206 (1985).
- ¹⁷M. Stuke, *Appl. Phys. Lett.* **45**, 1175 (1984); P. D. Brewer (private communication).
- ¹⁸C. D. Stinespring and A. Freedman, *Chem. Phys. Lett.* **143**, 584 (1988).
- ¹⁹D. Burgess, P. C. Stair, and E. Weitz, *J. Vac. Sci. Technol. A* **4**, 1362 (1986); P. C. Stair and E. Weitz, *J. Opt. Soc. Am. B* **4**, 255 (1987).
- ²⁰C. D. Wagner, in *Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy*, edited by D. Briggs (Heyden, London, 1977), pp. 114 and 122.
- ²¹M. K. Bahl, R. L. Watson, and K. J. Irgolic, *J. Chem. Phys.* **66**, 5526 (1977).
- ²²K. Siegbahn, C. Nording, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsalienis* **4**, 20 (1967).
- ²³U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Mannes, R. Nordberg, C. Nording, and K. Siegbahn, *Phys. Scr.* **2**, 70 (1970).
- ²⁴P. J. Young, R. K. Gosavi, J. Connor, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.* **58**, 5280 (1973).

SURFACE CHEMISTRY OF DIMETHYL CADMIUM AND DIMETHYL TELLURIUM AT 295 K

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Surface reactions of dimethyl cadmium and dimethyl tellurium on Au, GaAs(100), Si(100), and SiO₂ substrates at 295 K have been investigated. These studies followed UHV procedures and used X-ray photoelectron spectroscopy to characterize the chemical state of the surface reaction products. The results showed that both dimethyl cadmium and dimethyl tellurium form physisorbed and dissociatively chemisorbed adspecies with the specific reaction product distribution depending on the substrate. The sticking coefficient for dimethyl tellurium on GaAs was two orders of magnitude less than that for dimethyl cadmium. These observations are discussed in terms of simple electron transfer and covalent mechanisms for the surface interaction.

1. Introduction

Gas-surface reactions involving metal alkyls are of interest because of their importance in a variety of laser-assisted and thermal deposition techniques for metals and compound semiconductors. Ehrlich and Osgood [1], in an investigation of the UV photolysis of adsorbed van der Waals molecular films, have demonstrated laser-assisted chemical vapor deposition (LCVD) of aluminum and cadmium using trimethyl aluminum and dimethyl cadmium. More recently, Donnelly and co-workers [2] have demonstrated LCVD of GaAs using trimethyl gallium and trimethyl arsenic. Tokumitsu et al. [3] have employed organometallic-molecular beam epitaxy (OM-MBE) to deposit GaAs using trimethyl gallium and arsine, and Nishizawa et al. [4,5], using a laser-assisted technique termed molecular layer epitaxy (MLE), have also deposited GaAs.

Each of the cited processes, LCVD, OM-MBE, and MLE, involves the interaction of a metal alkyl with the substrate or growing thin film. The thermal surface chemistry of these molecules determines the nature of the surface with which subsequent metal alkyls must interact and, in certain cases, provides the adspecies with which incident photons must interact. Despite their importance, however, little direct information is available on these surface reactions.

This paper reports the results of an investigation

of the room temperature thermal surface chemistry of two metal alkyls, dimethyl cadmium and dimethyl tellurium, on metal, semiconductor, and insulator substrates. In the following sections, the experimental approach and results are described. The results are then discussed in terms of a general model for the surface reaction.

2. Experimental approach

The apparatus used in these studies consisted of an ultrahigh vacuum reaction cell interfaced directly to a Physical Electronics Inc. (PHI) surface analysis system via a gate valve. Samples were transferred between the analysis chamber and reaction cell using a magnetic transfer device. The general experimental procedure involved exposing a substrate to either dimethyl cadmium or dimethyl tellurium by backfilling the reaction cell to a given pressure (e.g. 1×10^{-6} Torr) for a specified time. The reaction cell was then evacuated and the exposed sample transferred to the adjacent chamber for analysis using X-ray photoelectron spectroscopy (XPS). This provided a determination of both the chemical state and surface coverage of the adsorbed species. Following the XPS analysis, the sample could be returned to the reaction cell, and the exposure/analysis cycle could be repeated. A detailed description of this apparatus is

given elsewhere [6]. Throughout the course of the reaction, the sample was maintained at 295 K. The dimethyl cadmium and dimethyl tellurium were supplied by Alfa Products and were used without further purification.

The surfaces studied in this work included GaAs(100), Si(100), SiO₂, and Au. The GaAs(100) and Si(100) samples were p-type electronic grade single crystal substrates supplied by Litton and Monsanto, respectively. The SiO₂ sample was an amorphous quartz plate, and the Au sample was a polycrystalline foil supplied by Alfa. All samples were cleaned by Ar⁺ ion etching (1 kV ion beam). The GaAs(100) and Si(100) samples were also annealed at 850 and 1100 K, respectively, to remove ion-induced damage and restore crystal order [7,8].

The XPS analyses were performed using a PHI 15 kV, Mg K α X-ray source and a PHI double pass cylindrical mirror electron energy analyzer operated at a pass energy of 50 eV. The analyzer was calibrated using the Au 4f_{7/2} photoelectron peak at 83.8 eV. For the SiO₂ surface, sample charging effects were taken into account by referencing the spectra to the Si 2p photoelectron peak at 103.4 eV.

The intensities, as well as the binding energies, of the adspecies XPS peaks provide useful information. For species present on the surface at monolayer and lower levels, the intensities of XPS peaks are directly proportional to the surface coverage, and calculational techniques developed by Madey et al. [9] may be used to determine this coverage from known values of X-ray mass absorption coefficients, electron mean free paths, and measured peak intensities. Finally, following Wedler and Klemperer [10], reactive sticking coefficients (i.e. for non-desorbing species) may be determined from the slope of coverage versus exposure measurements.

3. Results

XPS analyses of the Cd and Te 3d_{5/2} peaks for adspecies on the various substrates led to the identification of three distinct binding energies for each peak. These are summarized in table 1. Within the experimental uncertainty of ± 0.2 eV, the peaks at 404.6 and 572.6 eV correspond well with cadmium [11] and tellurium [12] metal. Based on studies of

Table 1

Observed Te and Cd 3d_{5/2} XPS peak binding energies and adspecies assignments

Binding energy (eV)		Adspecies assignment
Cd 3d _{5/2}	Te 3d _{5/2}	
404.6	572.6	metal
405.1	573.1	monomethyl
405.5	573.6	dimethyl

tellurium compounds (solids at 295 K) by Bahl et al. [12] and on electronegativity and ligand shift arguments for the analogous cadmium compounds [13,14], the remaining peaks may be associated with monomethyl and dimethyl species. These assignments are indicated in table 1.

Fig. 1 shows the Cd 3d photoelectron peaks for dimethyl cadmium adsorbed on Au, Si(100), SiO₂, and GaAs(100). The representative spectra shown here correspond to a dimethyl cadmium exposure of 5×10^{17} cm⁻². The intensities of the Cd 3d peaks

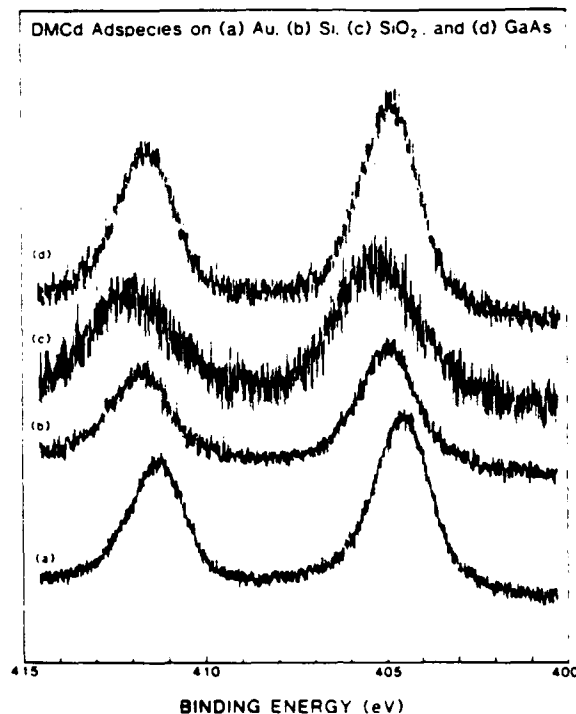


Fig. 1. Cd 3d XPS spectra for (a) Au, (b) Si, (c) SiO₂, and (d) GaAs exposed to 5×10^{17} cm⁻² dimethyl cadmium molecules at 295 K.

Table 2
Summary of observed adspecies

Substrate	Adspecies	
	Cd	Te
Au	Cd	(CH ₃) ₂ Te + Te
GaAs(100)	(CH ₃)Cd	(CH ₃)Te + Te
Si(100)	(CH ₃)Cd	-
SiO ₂	(CH ₃) ₂ Cd	-

shown in fig. 1 correspond to cadmium adspecies coverages on the order of 6.5×10^{14} , 9.7×10^{13} , 2.2×10^{13} , and $1.9 \times 10^{14} \text{ cm}^{-2}$ for Au, Si(100), SiO₂, and GaAs(100), respectively. It should be emphasized that the observed binding energies were independent of exposure and coverage. The cadmium adspecies identity, based on these spectra and the peak assignments given in table 1, are summarized in table 2. As indicated, physisorbed and dissociatively chemisorbed adspecies were observed.

Corresponding analyses of the Te 3d photoelectron peaks were used to establish the identity and coverage of Te adspecies resulting from dimethyl tellurium adsorption. A representative Te 3d_{5/2} spectrum corresponding to a dimethyl tellurium exposure of $4 \times 10^{16} \text{ cm}^{-2}$ on Au is shown in fig. 2. This peak has been decomposed to show major contributions from physisorbed dimethyl tellurium (573.6 eV) and tellurium metal (572.6 eV). The low level peak at

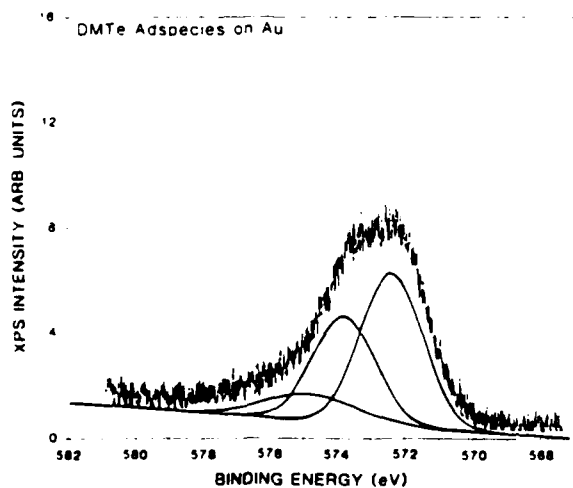


Fig. 2. Te 3d_{5/2} XPS spectrum for Au exposed to $4 \times 10^{16} \text{ cm}^{-2}$ dimethyl tellurium molecules at 295 K.

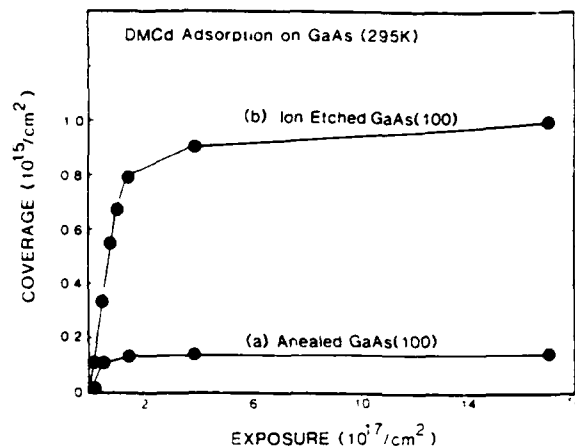


Fig. 3. Plot of cadmium adspecies surface coverage versus exposure for (a) GaAs(100) and (b) unannealed GaAs(100) previously exposed to a fluence of $2 \times 10^{17} \text{ cm}^{-2}$ 1 kV Ar⁺ ions.

approximately 575 eV is an X-ray satellite associated with the Te 3d_{3/2} peak. The total adspecies coverage represented here is on the order of $3.9 \times 10^{14} \text{ m}^{-2}$. Similar analyses for the exposed GaAs substrate revealed the presence of low levels of monomethyl tellurium and tellurium metal, and because of even more limited dimethyl tellurium uptake on Si and SiO₂, no data for tellurium adspecies on these surfaces were obtained. These results along with those for cadmium adspecies are summarized for each surface in table 2.

Measurements of adspecies coverage as a function of exposure to dimethyl cadmium and dimethyl tellurium were performed for the GaAs(100) substrate. Typical results of these measurements for dimethyl cadmium are shown in fig. 3. Also shown in fig. 3 is a corresponding plot for dimethyl cadmium uptake on an unannealed GaAs surface previously exposed to $2 \times 10^{17} \text{ m}^{-2}$ 1 kV Ar⁺ ions. From these data, it appears that ion-induced damage increases the saturation surface coverage without substantially altering the initial reactive sticking coefficient. This is on the order of 7×10^{-3} for the clean GaAs surface and becomes essentially zero as the coverage approaches saturation. For dimethyl tellurium, comparable measurements showed that the reactive sticking coefficient on GaAs was on the order of 3×10^{-3} .

The chemical state and coverage of carbon produced by the surface reactions of the metal alkyls was monitored using the C 1s XPs peak. For Au, traces

of carbon in a hydrocarbon or graphitic state were observed. For Si and SiO₂, multiple carbon species including SiC were observed. The carbon coverage for these surfaces was always on the order of two times the metal species coverage. For the GaAs surface, the C 1s photoelectron peak obtained using the Mg K α X-ray source lies in the same spectral region as a Ga LMM Auger peak. This interference, combined with the relatively low C 1s cross section and generally low adspecies coverages, essentially precluded the acquisition of useful chemical state information for carbon on GaAs.

4. Discussion

The results of this study provide two important observations concerning the surface reactions of dimethyl cadmium and dimethyl tellurium at 295 K. The first is the adspecies identity and the second concerns the sticking coefficients. Insight into both may be provided by an understanding of the electronic structure of the incident molecule and its possible interactions with the surface.

The low sticking coefficients observed for dimethyl tellurium on GaAs surfaces can be ascribed to the fact that it is a closed shell molecule with a full complement of s, p, and d electrons. Long range electron transfer interactions with the surface are virtually precluded by the fact that such molecules tend to have vanishing small or even negative electron affinities. This reduces the possibility of electron transfer at large impact parameters. Any interaction of dimethyl tellurium with the substrate on the covalent potential energy surface is probably limited to short range interactions through lone pair electrons on the tellurium atom. In this case, the interaction may be similar to that for water, an analogous closed shell molecule, which is known to have very low room temperature sticking coefficients and to form both physisorbed and chemisorbed adspecies on various GaAs and Si surfaces [15].

Dimethyl cadmium, although having a fully saturated valence (fully paired d orbitals and bonded s orbital electrons), contains three empty low-lying p orbitals on the cadmium atom which are available for accepting an electron from the substrate. Thus, for GaAs, whose low work function (4.7 eV [16])

would facilitate long range electron transfer, one might expect relatively large sticking coefficients. However, according to Walsh's rules [17], the dimethyl cadmium negative ion should be bent, while the neutral molecule is linear. In the limit that electron transfer occurs by a vertical transition, the orbital overlap (Franck-Condon factor) will be small, limiting the reaction probability. This could explain the comparatively small sticking coefficients found in this study (10^{-2} to 10^{-3}). A classic example of this type of behavior is provided by the linear nitrous oxide molecule, whose reactive scattering (with barium) [18,19] and dissociative electron attachment cross sections [20] are greatly enhanced by energy input into its vibrational bending modes.

The dissociative chemisorption of dimethyl cadmium also seems to be correlated with the strength of the long range electron transfer mechanism. On GaAs, whose low work function facilitates electron transfer, dimethyl cadmium chemisorbs. Similar results are obtained for the Au and Si surfaces, which also have work functions of approximately 4 eV [21,22]. On SiO₂, an insulator (valence band maximum \approx 10 eV and band gap \approx 9 eV [23]) for which electron transfer should be inhibited, physisorbed cadmium adspecies are observed.

A complete understanding of the reaction mechanism and subsequent chemical bonding requires experimental and theoretical results well beyond the scope of those presented here. Other factors that need to be examined include: crystal orientation, surface structure, adspecies-adspecies interactions, surface defects, and doping effects. For example, the presence of metallic tellurium on Au and GaAs may be due to adspecies-adspecies interactions. Tellurium dimer bond energies are on the order of twenty times greater than those for cadmium, and this may provide the driving force for dimethyl tellurium decomposition on Au and GaAs. Similarly, ion-induced surface damage appears to increase the saturation coverage substantially for dimethyl cadmium adspecies on GaAs, which suggests the importance of surface defects.

5. Conclusions

This study has shown that the thermal surface reactions of dimethyl cadmium and dimethyl tellur-

ium at 295 K on Au, GaAs(100), Si(100), and SiO₂ produce both physisorbed and dissociatively chemisorbed adspecies. The identity of the adspecies depends on the nature of the substrate and the reacting molecule. These surface interactions are also characterized by low reactive sticking coefficients and saturation surface coverages. A complete understanding of the relevant surface chemistry will require additional work on both the experimental and theoretical aspects of these surface interactions. The effects of key parameters, surface orientation, structure, and temperature as well as central atom identity (e.g., Zn, Cd, or Hg) and ligand group (electron donating versus electron withdrawing) of the adsorbing molecule, remain to be studied. Because of the importance of metal alkyl-surface interactions in thermal and photon-assisted deposition processes, studies of these effects are planned for the near future. Initial studies of the adspecies photochemistry have been completed and will be reported elsewhere [24].

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References

- [1] D.J. Ehrlich and R.M. Osgood Jr., *Chem. Phys. Letters* 79 (1981) 381.
- [2] V.M. Donnelly, V.R. McCarty, A. Appelbaum, D. Brasen and W.P. Lowe, *J. Appl. Phys.* 61 (1987) 1410.
- [3] E. Tokumitsu, Y. Kurow, M. Kanogai and K. Takahashi, *J. Appl. Phys.* 55 (1984) 3163.
- [4] J. Nishizawa, H. Abe and T. Kurabayashi, *J. Electrochem. Soc.* 132 (1985) 1199, 1939.
- [5] J. Nishizawa, K.T. Kurabayashi, H. Abe and N. Sakurai, *J. Vacuum Sci. Technol.*, to be published.
- [6] C.D. Stinespring and A. Freedman, *J. Vacuum Sci. Technol.* 4 (1986) 1946; *Appl. Phys. Letters* 48 (1986) 718.
- [7] M. Henzler, *Surface Sci.* 36 (1973) 109.
- [8] L.A. Kolodziejski, R.L. Gunshor, N. Otsuka, S. Datta, W.M. Becker and A.V. Nurmikko, *IEEE J. Quantum Electron.* QE-22 (1986) 1666.
- [9] T.E. Mady, J.T. Yates and N.E. Erickson, *Chem. Phys. Letters* 19 (1973) 487.
- [10] G. Wedler and W.F. Klemperer, *Chemisorption: an experimental approach* (Butterworths, London, 1976).
- [11] C.D. Wagner, in: *Handbook of X-ray and ultraviolet photoelectron spectroscopy*, ed. D. Briggs (Heyden, London, 1977).
- [12] M.K. Bahl, R.L. Watson and K.J. Irgolic, *J. Chem. Phys.* 66 (1977) 5526.
- [13] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.E. Karlsson, I. Lindgren and B. Lindberg, *Electron spectroscopy for chemical analysis - atomic, molecular, and solid state structure studied by means of electron spectroscopy* (Almqvist and Wiksell, Stockholm, 1967); *Nova Acta Regiae Soc. Sci. Upsalienis Ser. IV* (1967) 20.
- [14] U. Gelius, P.F. Heden, J. Hedman, B.J. Lindberg, R. Mannes, R. Nordberg, C. Nordling and K. Siegbahn, *Physica Scripta* 2 (1970) 70.
- [15] P.A. Thiel and T.E. Madey, *Surface Sci. Rept.* 7 (1987) 211.
- [16] J. van Laar, A. Huijser and T.L. van Rooy, *J. Vacuum Sci. Technol.* 14 (1977) 894.
- [17] J. Walsh, *J. Chem. Soc.* (1953) 2260.
- [18] D.J. Wren and M. Menzinger, *J. Chem. Phys.* 63 (1975) 4557; *Faraday Discussions Chem. Soc.* 67 (1979) 97.
- [19] H. Jalink, F. Harren, D. van den Ende and S. Stolte, *Chem. Phys.* 108 (1981) 391.
- [20] J.N. Bardsley, *J. Chem. Phys.* 51 (1969) 3385, and references therein.
- [21] I. Ameiser, *Z. Physik* 69 (1931) 111.
- [22] L. Esaki, *J. Phys. Soc. Japan* 8 (1953) 347.
- [23] T.D. Stefano and D.E. Eastman, *Phys. Rev. Letters* 27 (1971) 1560.
- [24] C.D. Stinespring and A. Freedman, *Appl. Phys. Letters*, submitted for publication.

**LASER INDUCED SURFACE CHEMICAL
EPITAXY OF II-VI MATERIALS**

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LASER INDUCED SURFACE CHEMICAL EPITAXY OF II-VI MATERIALS

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ABSTRACT

Studies of the thermal and photon-induced surface chemistry of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe) on GaAs(100) substrates under ultrahigh vacuum conditions have been performed for substrate temperatures in the range of 123 K to 473 K. Results indicate that extremely efficient conversion of admixtures of DMTe and DMCd to CdTe can be obtained using low power ($5 - 10 \text{ mJ cm}^{-2}$) 193 nm laser pulses at substrate temperatures of 123 K. Subsequent annealing at 473 K produces an epitaxial film.

INTRODUCTION

Thermal and photon-assisted deposition processes involving organometallic precursor species are currently being investigated for II-VI and III-V compound semiconductors.[1] These processes provide the potential for reduced growth temperatures and increased process flexibility. Illustrations include reduced pressure laser assisted chemical vapor deposition (LCVD) of CdTe[2] and ultra high vacuum (UHV) metalorganic molecular beam epitaxy (MOMBE) of GaAs.[3] These relatively new deposition processes raise important questions concerning chemical mechanisms which must be answered if the processes and materials they produce are to be optimized.

This paper describes ongoing experimental studies[4,5] of the thermal and photon-induced surface reactions of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe). The objectives of these studies are to provide an understanding of the underlying chemical and physical processes and to explore novel approaches to CdTe heteroepitaxy. The work focuses on CdTe heteroepitaxy because of the the importance of this material in electro-optical systems.[6] DMCd and DMTe were the first precursor species selected for investigation because of their inherent scientific interest. The gas phase photochemistry of DMCd and DMTe has been extensively investigated; these molecules are known to undergo one photon dissociation to produce ground state metal atoms.[7-9] This behavior contrasts with that of trimethyl gallium and trimethyl arsenic which dissociate in the gas phase via a multiphoton excitation process.[10] The basic question is how can the photophysics of these molecules be used to obtain CdTe thin films.

EXPERIMENTAL

The experimental apparatus used in these studies is shown in Figure 1. It consists of a turbomolecular pumped, liquid nitrogen trapped UHV reaction cell interfaced to an ion/sublimation pumped UHV analysis chamber. The diagnostics used in these studies are X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). The sample is transferred between chambers using a linear motion feedthrough with sample heating (1200 K) and cooling (123 K) capabilities. Samples are exposed to

reactive gas species using an effusive molecular beam doser. For the sample-source geometry used here, the angular distribution of the effusive beam produced only a nominal 10% variation in exposure over the analyzed area of the surface. Photon-induced processes were studied by irradiating the surface with UV photons produced by an excimer laser. These were introduced through a Conflat mounted MgF_2 window (Harshaw). The wavelengths used in these experiments were 193 nm, 248 nm, and 351 nm. Laser fluence, controlled using a simple beam expander, ranged from 0.3 mJ cm^{-2} to 6.0 mJ cm^{-2} to minimize the effects of surface heating ($<3 \text{ K}$ to 60 K)[11].

The GaAs samples used in these studies were p-type electronic grade single crystal substrates provided by Litton. In situ sample cleaning involved Ar^+ ion etching at 1 kV until no trace of oxygen contamination could be observed. This was followed by annealing at 850 K[12] to restore surface order (as observed by LEED). The DMCd and DMTe (Alfa) were purified using a series of freeze-thaw cycles.

The XPS analyses were performed using a PHI 15 kV, Mg K_α source and a PHI double pass cylindrical mirror electron energy analyzer operated at a pass energy of 25 eV. The analyzer was calibrated using the $\text{Au } 4f_{7/2}$ peak at 83.8 eV. All spectra were referenced to the $\text{Ga } 3d_{5/2}$ peak at 18.8 eV. No charging effects were observed except in the limit of very thick films. ($> 200 \text{ \AA}$).

RESULTS AND DISCUSSION

As discussed elsewhere[4], XPS analyses of the Cd and Te $3d_{5/2}$ peaks can indicate the nature of the chemical bonding of the metalorganic species on the GaAs surface. The interaction of the adspecies with the surface follows what one might expect from the chemical structure of the metal alkyl. DMTe, a closed shell molecule, has a lower sticking coefficient than DMCd at all temperatures. Furthermore, at 123 K where no thermal dissociation takes place for either molecule, the characteristic Te peak does not shift as adspecies coverage increases from sub-monolayer to multilayer coverage. This would indicate that DMTe does not strongly interact with the GaAs surface. The Cd peak from DMCd, on the other hand,

APPARATUS USED in STUDIES of SEMICONDUCTOR EPITAXY

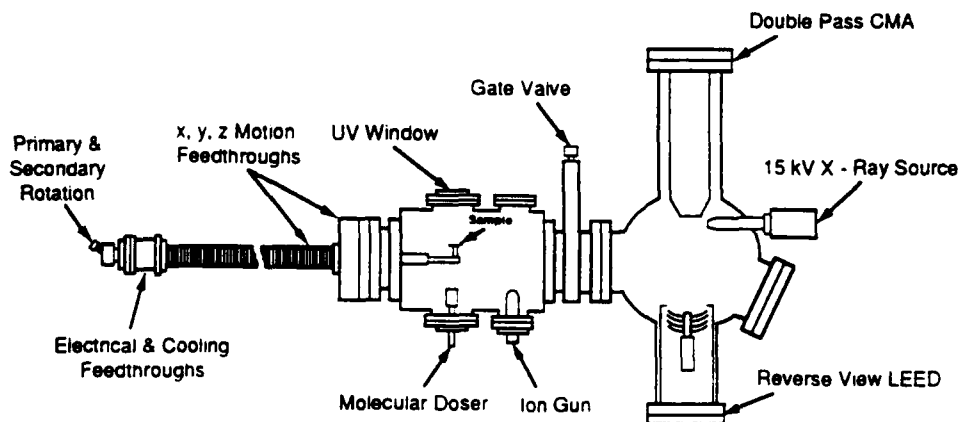


Figure 1. Cross sectional view of deposition and analysis system.

undergoes a several eV shift to higher bonding energies as coverage increases. The surface induced shift to low binding energies is consistent with electron flow from the GaAs to the vacant 3 p orbitals on the Cd atom.

A discussion of the photoinduced chemistry of submonolayer to monolayer coverages is beyond the scope of this paper but will be reported elsewhere[13]. In summary, the photochemistry is dominated by surface-mediated effects for GaAs even at 123 K, in contrast to the results obtained on quartz substrates[5]. It is difficult to cleanly photodissociate either DMTe or DMCd to metal atoms at 193 nm and 248 nm, even though the gas phase photochemistry produces cleavage of both metal-alkyl bonds. Irradiation produces a distribution of metal, dimethyl, and monomethyl species which varies with the total dose of laser photons.

Since our aim was to produce CdTe thin films at low temperatures, we began to use multilayer coverages (100-200 Å), which should have the effect of minimizing surface-induced effects. The result of irradiating thick (200 Å) admixtures of DMTe and DMCd with 193 nm photons is the production of CdTe thin films with stoichiometric ratios. Figure 2 shows the XPS signal from the Te 3d_{5/2} state as a function of laser dose. The rather broad spectrum of the unreacted film is immediately converted to a narrow peak at a binding energy indicative of metallic tellurium. Thermal annealing of the irradiated film produces cadmium telluride. Similar results are obtained when viewing the cadmium spectra. Figure 3 presents typical carbon 1s XPS spectra. The top spectrum shows two distinct peaks; based on single compound exposure, one is identifiable as carbon from DMTe (higher binding energy) and one as carbon from DMCd. Upon irradiation of 150 laser pulses at 193 nm (9×10^{17} photons total dose), all the carbon is converted to a new species (lower spectrum), whose binding energy is consistent with hydrocarbon production.

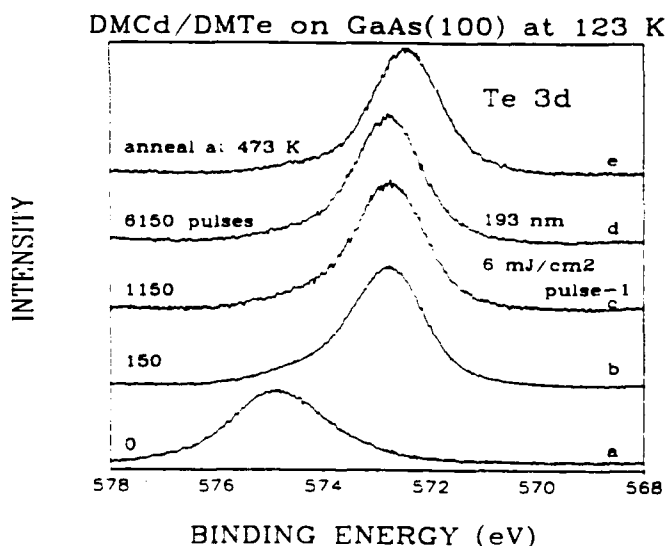


Figure 2. XPS spectra of the Te 3d_{5/2} peak of an ~100Å thick film of a DMTe/DMCd mixture on a GaAs(100) substrate at 123 K as a function of the number of 193 nm laser pulses at 6 mJ cm⁻¹. The top spectrum is the result of a subsequent thermal anneal at 473 K.

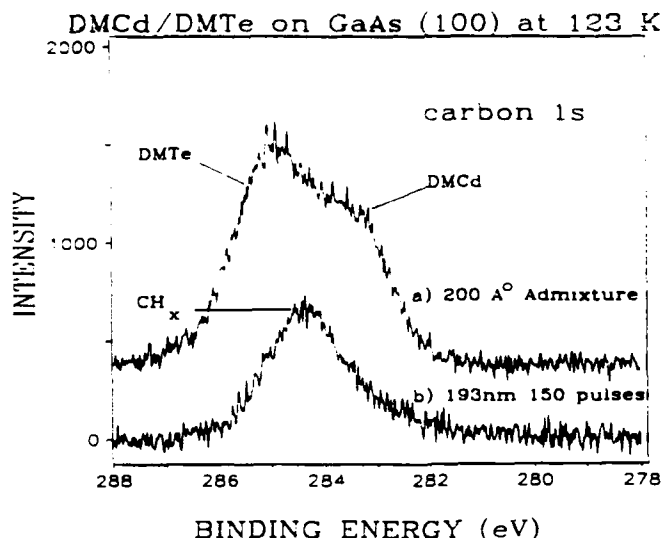


Figure 3. XPS spectra of the C 1s peak of a DMTe/DMCd admixture at a GaAs substrate temperature of 123 K before a) and after b) irradiation by 150 pulses at 6 mJ cm^{-2} of an ArF excimer laser operating at 193 nm.

Similar results are obtained no matter what the initial stoichiometry of the non-irradiated thin film. Cadmium to tellurium ratios of 0.5 to 2.0 always produced stoichiometric CdTe thin films with no excess of one species or the other. These results imply that the laser irradiation initiated a chemical reaction between the two metal alkyls, with any excess reactant being driven off the surface. The question arises as to whether this effect is due to the properties of the thin film or just to substrate heating effects. The films were therefore irradiated with 6 mJ cm^{-2} pulses from a XeF laser operating at 351 nm. At this wavelength, the thin film should be transparent. Figure 4 presents spectra of the Te $3d_{5/2}$ XPS peak for 351 vs. 193 nm. Clearly, the 351 nm laser pulses are not effective in inducing a chemical reaction. Thus the observed results are consistent with the energy being absorbed in the thin film; whether the reaction is catalyzed by photo-induced or electronically excited reactants or free radicals, increased precursor mobility, and/or thermal excitation cannot be deduced from the data.

We note that the CdTe films produced by 193 nm laser irradiation are heavily contaminated with carbon. Subsequent laser irradiation slowly reduces the level of carbon contamination but only annealing at 473 K for twenty minutes reduces carbon levels below detection limits ($\sim 0.5\%$). Upon annealing, we observe a 1×1 LEED pattern for the CdTe(100) surface indicating the presence of an epitaxial CdTe thin film. XPS indicates that the resultant film is on the order of 100\AA thick.

CONCLUSIONS

An epitaxial thin film ($\sim 100\text{\AA}$) of CdTe on GaAs(100) has been produced by 193 nm photon irradiation of beam deposited admixtures of dimethyl tellurium and cadmium at substrate temperatures of 123 K followed by a thermal anneal at 473 K. The resultant LEED pattern is 1×1 indicating an epitaxial (100) CdTe surface. The process is quite

DMCd/DMTe on GaAs (100) at 123 K

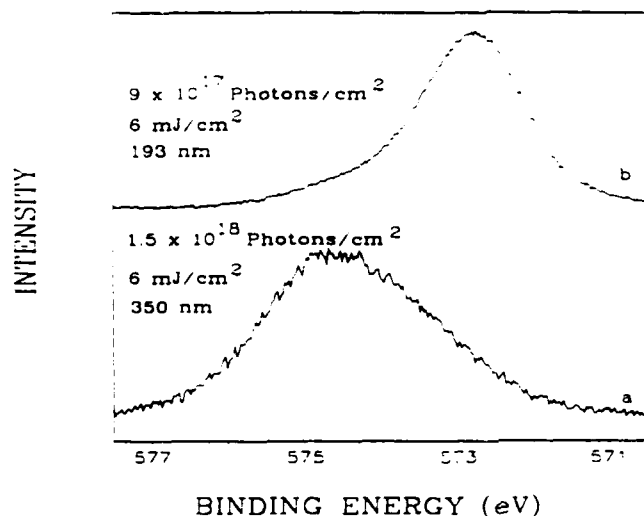


Figure 4. XPS spectra of the Te 3d_{5/2} peak upon irradiation at a) 351 nm and b) 193 nm for equal per pulse fluence and total energy dose. Film and substrate conditions are the same as in Figures 2 and 3.

efficient at laser fluences of $\sim 6 \text{ mJ cm}^{-2}$; lower fluences or much longer wavelengths (351 nm) are not effective. The process is linked to the absorption of photons in the thin film leading to a chemical reaction between the molecular species to produce CdTe and a hydrocarbon species.

The advantages of making II-VI compound semiconductors by this technique are apparent. By using a cold GaAs (123 K) substrate, we have increased sticking coefficients to .1 - .3, two to three orders of magnitude greater than that found at typical growth temperatures (500-600 K), thus saving on usage of metal alkyl precursors. Another potential advantage is the photo-induced "fixing" of the chemical reaction to produce CdTe, which opens the way to patterned deposition with reasonably fine resolution. A drawback at this point is the need to anneal the sample of 473 K to remove the carbon contamination and produce epitaxial ordering. But, if pulsed laser annealing could be utilized, this problem could be overcome. Future work is indicated in the area of ternary compounds, such as HgCdTe. Dimethyl mercury also absorbs strongly at 193 nm and thus is a candidate for laser surface chemical epitaxy.

ACKNOWLEDGEMENTS

This research was sponsored by the Air Force Office of Scientific Research under Small Business Innovative Research Program Contract No. F49620-86-C-0089.

REFERENCES

1. J.A. O'Neill, P. Shaw, E. Sanchez, Z. Wu and R.M. Osgood, Jr., "Surface Spectroscopic Studies of Organometallic Deposition," *Mat. Res. Soc. Symp.*, Vol. 129, (1989).
2. J.J. Zinck, P.D. Brewer, J.E. Jensen, G.L. Olsen and L.W. Tuh, *Appl. Phys. Lett.* **52**, 1434 (1988); J.B. Mullin and S.J.C. Irvine, *J. Vac. Sci. Technol.* **A4**, 700 (1986).
3. E. Tokumitsu, Y. Kurow, M. Kanogai and K. Takahashi, *J. Appl. Phys.* **55**, 3163 (1984).
4. C.D. Stinespring and A. Freedman, *Chem. Phys. Lett.* **143**, 584 (1988).
5. C.D. Stinespring and A. Freedman, *Appl. Phys. Lett.* **52**, 1959 (1988).
6. R.A. Wood and R.J. Hager, *J. Vac. Sci. Technol.* **A1**, 1608 (1983).
7. C. Jonah, P. Chandra, and R. Bersohn, *J. Chem Phys.* **55**, 1903 (1971), C.F. Yu, F. Youngs, K. Tsukiyama, R. Bersohn, and J. Preses, *J. Chem. Phys.* **85**, 1382 (1986).
8. C.J. Chen and R.M. Osgood, *J. Chem. Phys.* **81**, 327 (1984).
9. P.D. Brewer, J.E. Jensen, G.L. Olsen, L.W. Tutt and J.J. Zinck, *Proc. Mat. Res. Soc. Symp.* **101**, 327 (1988); P.D. Brewer, *Chem. Phys. Lett.*, **141**, 301 (1987).
10. V.M. Donnelly, J.A. McCauley, V.R. McCrary, C.W. Tu and J.C. Beggy, "Selective Area Growth of GaAs by Laser Induced Pyrolysis of Absorbed Gallium-Alkyls," *Proc. Mat. Res. Soc. Symp.*, Vol. 129 (1989).
11. D. Burgess, P.C. Stair, and E. Weitz, *J. Vac. Sci. Technol.* **A4**, 1362 (1986); P.C. Stair and E. Weitz, *J. Opt. Soc. Am.* **B4**, 255 (1987).
12. L.A. Kolodziejski, R.L. Gunshor, N. Otsuka, S. Datta, W.M. Becker and A.V. Nurmikko, *IEEE J. Quantum Electron.* **QE-22**, 1666 (1986).
13. Manuscript in preparation.

Laser induced surface chemical epitaxy

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ABSTRACT

Studies of the thermal and photon-induced surface chemistry of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe) on GaAs(100) substrates under ultrahigh vacuum conditions have been performed for substrate temperatures in the range of 123 K to 473 K. Results indicate that extremely efficient conversion of admixtures of DMTe and DMCd to CdTe can be obtained using low power ($5 - 10 \text{ mJ cm}^{-2}$) 193 nm laser pulses at substrate temperatures of 123 K. Subsequent annealing at 473 K produces an epitaxial film.

1. INTRODUCTION

Thermal and photon-assisted deposition processes involving organometallic precursor species are currently being investigated for II-VI and III-V compound semiconductors.[1] These processes provide the potential for reduced growth temperatures and increased process flexibility. Illustrations include reduced pressure laser assisted chemical vapor deposition (LCVD) of CdTe[2] and ultra high vacuum (UHV) metalorganic molecular beam epitaxy (MOMBE) of GaAs.[3] These relatively new deposition processes raise important questions concerning chemical mechanisms which must be answered if the processes and materials they produce are to be optimized.

This paper describes ongoing experimental studies[4,5] of the thermal and photon-induced surface reactions of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe). The objectives of these studies are to provide an understanding of the underlying chemical and physical processes and to explore novel approaches to CdTe heteroepitaxy. The work focuses on CdTe heteroepitaxy because of the the importance of this material in electro-optical systems.[6] DMCd and DMTe were the first precursor species selected for investigation because of their inherent scientific interest. The gas phase photochemistry of DMCd and DMTe has been extensively investigated; these molecules are known to undergo one photon dissociation to produce ground state metal atoms.[7-9] This behavior contrasts with that of trimethyl gallium and trimethyl arsenic which dissociate in the gas phase via a multiphoton excitation process.[10] The basic questions we attempt to answer in this study are: i) How do DMCd and DMTe interact with the surface of a substrate or growing thin film? and ii) Is this interaction such that single photon (as opposed to multiphoton) processes can be used to produce metal adspecies and, ultimately, epitaxial CdTe thin films?

2. EXPERIMENTAL

The experimental apparatus used in these studies is shown in Figure 1. It consists of a turbomolecular pumped, liquid nitrogen trapped UHV reaction cell

APPARATUS USED in STUDIES of SEMICONDUCTOR EPITAXY

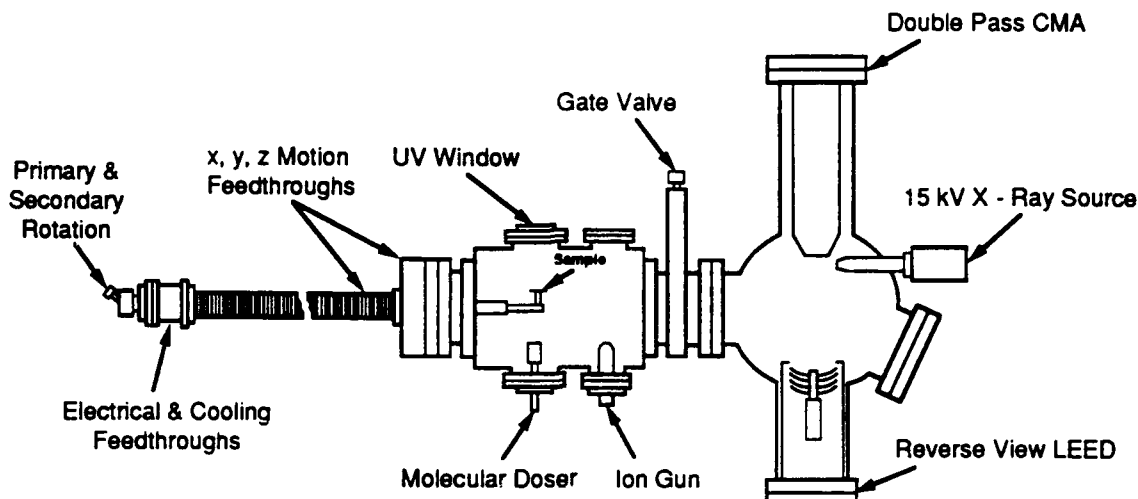


Figure 1. Cross sectional view of deposition and analysis system.

interfaced to an ion/sublimation pumped UHV analysis chamber. The diagnostics used in these studies are X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). The sample is transferred between chambers using a linear motion feedthrough with sample heating (1200 K) and cooling (123 K) capabilities. Samples are exposed to reactive gas species using an effusive molecular beam doser. For the sample-source geometry used here, the angular distribution of the effusive beam produced only a nominal 10% variation in exposure over the analyzed area of the surface. Photon-induced processes were studied by irradiating the surface with UV photons produced by an excimer laser. These were introduced through a Conflat mounted MgF_2 window (Harshaw). The wavelengths used in these experiments were 193 nm, 248 nm, and 351 nm. Laser fluence, controlled using a simple beam expander, ranged from 0.3 mJ cm^{-2} to 6.0 mJ cm^{-2} to minimize the effects of surface heating ($<3 \text{ K}$ to 60 K)[11].

The GaAs samples used in these studies were p-type electronic grade single crystal substrates provided by Litton. In situ sample cleaning involved Ar^+ ion etching at 1 kV until no trace of oxygen contamination could be observed. This was followed by annealing at 850 K[12] to restore surface order (as observed by LEED). The DMCd and DMTe (Alfa) were purified using a series of freeze-thaw cycles.

The XPS analyses were performed using a PHI 15 kV, $\text{Mg K}\alpha$ source and a PHI double pass cylindrical mirror electron energy analyzer operated at a pass energy of 25 eV. The analyzer was calibrated using the $\text{Au } 4f_{7/2}$ peak at 83.8 eV. All spectra were referenced to the $\text{Ga } 3d_{5/2}$ peak at 18.8 eV. No charging effects were observed except in the limit of very thick films. ($> 200 \text{ \AA}$).

3. RESULTS AND DISCUSSION

As discussed elsewhere[4], XPS analyses of the Cd and Te $3d_{5/2}$ peaks can indicate the nature of the chemical bonding of the metalorganic species on the GaAs surface. The interaction of the adspecies with the surface follows what one might expect from the chemical structure of the metal alkyl. DMTe, a closed shell molecule, has a lower sticking coefficient than DMCd at all temperatures. Furthermore, at 123 K where no thermal dissociation takes place for either molecule, the characteristic Te peak does not shift as adspecies coverage increases from sub-monolayer to multilayer coverage. This would indicate that DMTe does not strongly interact with the GaAs surface. The Cd peak from DMCd, on the other hand, undergoes a several eV shift to higher bonding energies as coverage increases. The surface induced shift to low binding energies is consistent with electron flow from the GaAs to the vacant 3 p orbitals on the Cd atom.

A discussion of the photoinduced chemistry of submonolayer to monolayer coverages is beyond the scope of this paper but will be reported elsewhere[13]. In summary, the photochemistry is dominated by surface-mediated effects for GaAs even at 123 K, in contrast to the results obtained on quartz substrates[5]. It is difficult to cleanly photodissociate either DMTe or DMCd to metal atoms at 193 nm and 248 nm, even though the gas phase photochemistry produces cleavage of both metal-alkyl bonds. Irradiation produces a distribution of metal, dimethyl, and monomethyl species which varies with the total dose of laser photons.

Since our aim was to produce CdTe thin films at low temperatures, we began to use multilayer coverages (100-200 Å), which should have the effect of minimizing surface-induced effects. The result of irradiating thick (200 Å) admixtures of DMTe and DMCd with 193 nm photons is the production of CdTe thin films with stoichiometric ratios. Figure 2 shows the XPS signal from the Te $3d_{5/2}$ state as a function of laser dose. The rather broad spectrum of the unreacted film is immediately converted to a narrow peak at a binding energy indicative of metallic tellurium. Thermal annealing of the irradiated film produces cadmium telluride. Similar results are obtained when viewing the cadmium spectra. Figure 3 presents typical carbon 1s XPS spectra. The top spectrum shows two distinct peaks; based on single compound exposure, one is identifiable as carbon from DMTe (higher binding energy) and one as carbon from DMCd. Upon irradiation of 150 laser pulses at 193 nm (9×10^{17} photons total dose), all the carbon is converted to a new species (lower spectrum), whose binding energy is consistent with hydrocarbon production.

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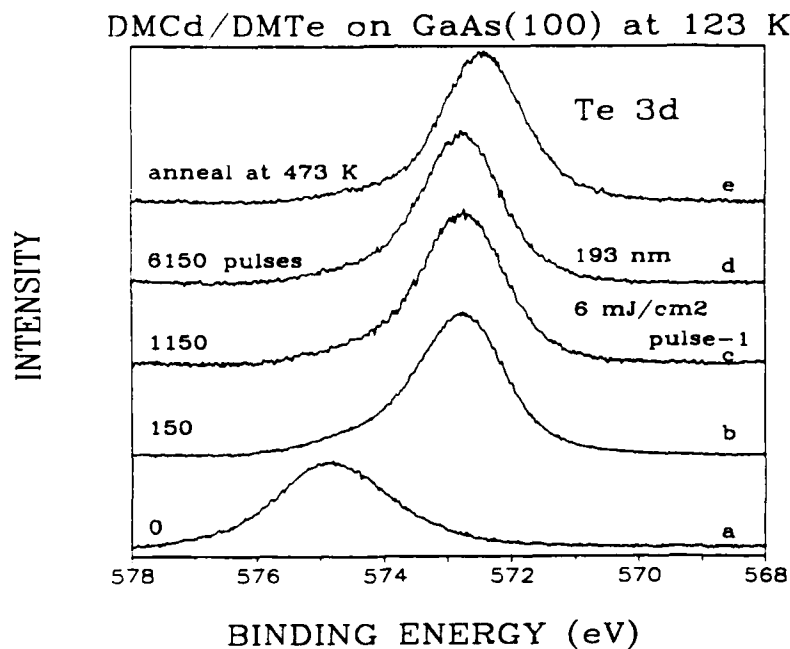


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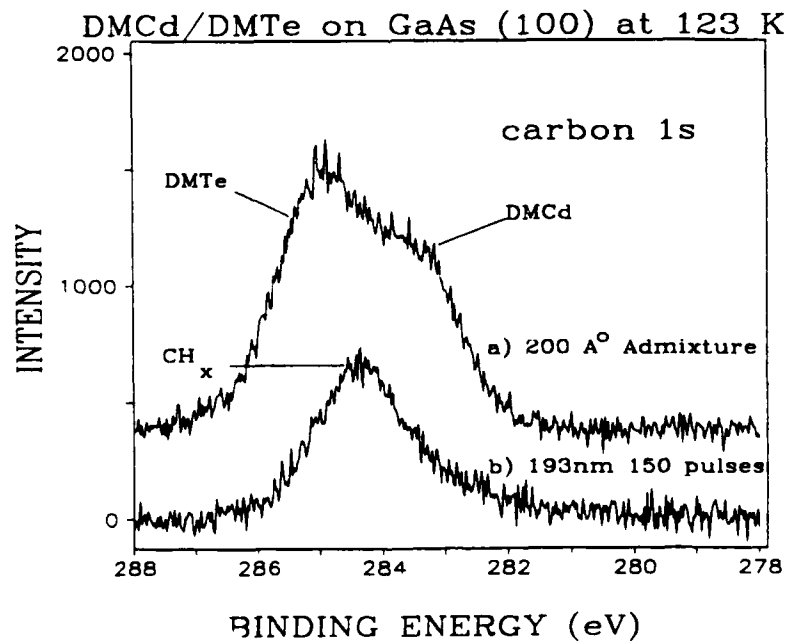


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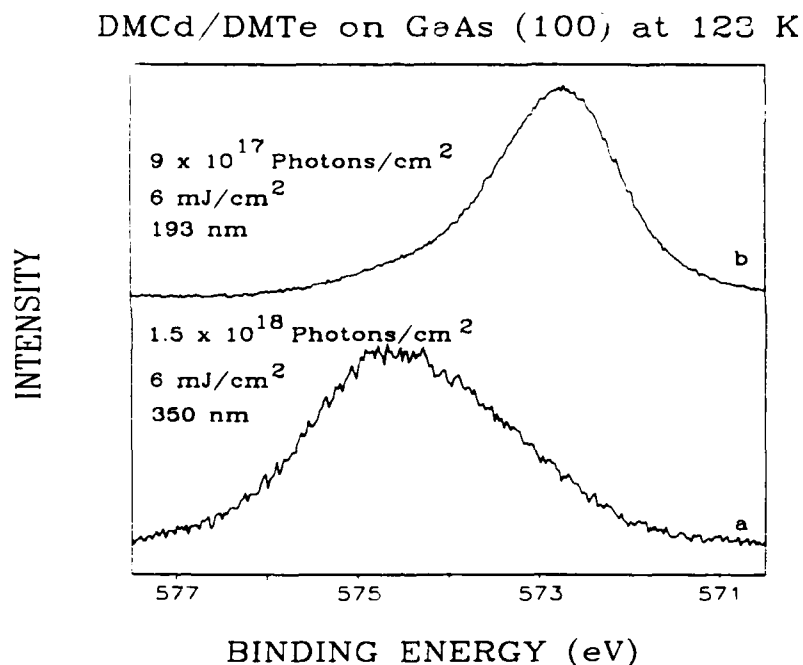


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4. CONCLUSIONS

An epitaxial thin film ($\sim 100\text{\AA}$) of CdTe on GaAs(100) has been produced by 193 nm photon irradiation of beam deposited admixtures of dimethyl tellurium and cadmium at substrate temperatures of 123 K followed by a thermal anneal at 473 K. The resultant LEED pattern is 1×1 indicating an epitaxial (100) CdTe surface. The process is quite efficient at laser fluences of $\sim 6 \text{ mJ cm}^{-2}$; lower fluences or much longer wavelengths (351 nm) are not effective. The process is linked to the absorption of photons in the thin film leading to a chemical reaction between the molecular species to produce CdTe and a hydrocarbon species.

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6. REFERENCES

1. J.A. O'Neill, P. Shaw, E. Sanchez, Z. Wu and R.M. Osgood, Jr., "Surface Spectroscopic Studies of Organometallic Deposition," Mat. Res. Soc. Symp., Vol. 129, (1989).
2. J.J. Zinck, P.D. Brewer, J.E. Jensen, G.L. Olsen and L.W. Tuh, Appl. Phys. Lett. 52, 1434 (1988); J.B. Mullin and S.J.C. Irvine, J. Vac. Sci. Technol. A4, 700 (1986)
3. E. Tokumitsu, Y. Kurow, M. Kanogai and K. Takahashi, J. Appl. Phys. 55, 3163 (1984).
4. C.D. Stinespring and A. Freedman, Chem. Phys. Lett 143, 584 (1988).
5. C.D. Stinespring and A. Freedman, Appl. Phys. Lett. 52, 1959 (1988).
6. R.A. Wood and R.J. Hager, J. Vac. Sci. Technol. A1, 1608 (1983).
7. C. Jonah, P. Chandra, and R. Bersohn, J. Chem Phys. 55, 1903 (1971), C.F. Yu, F. Youngs, K. Tsukiyama, R. Bersohn, and J. Preses, J. Chem. Phys. 85, 1382 (1986).
8. C.J. Chen and R.M. Osgood, J. Chem. Phys. 81, 327 (1984).
9. P.D. Brewer, J.E. Jensen, G.L. Olsen, L.W. Tutt and J.J. Zinck, Proc. Mat. Res. Soc. Symp. 101, 327 (1988); P.D. Brewer, Chem. Phys. Lett., 141, 301 (1987).
10. V.M. Donnelly, J.A. McCaulley, V.R. McCrary, C.W. Tu and J.C. Beggy, "Selective Area Growth of GaAs by Laser Induced Pyrolysis of Absorbed Gallium-Alkyls," Proc. Mat. Res. Soc. Symp., Vol. 129 (1989).
11. D. Burgess, P.C. Stair, and E. Weitz, J. Vac. Sci. Technol. A4, 1362 (1986); P.C. Stair and E. Weitz, J. Opt. Soc. Am. B4, 255 (1987).
12. L.A. Kolodziejski, R.L. Gunshor, N. Otsuka, S. Datta, W.M. Becker and A.V. Nurmikko, IEEE J. Quantum Electron. QE-22, 1666 (1986).
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Thermal and Photolytic Decomposition of Adsorbed Cadmium and Tellurium Alkyls

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ABSTRACT

Studies of the thermal and photon-induced surface chemistry of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe) under ultrahigh vacuum conditions have been performed for substrate temperatures in the range of 133 K to 295 K. Results on GaAs(100) and Si(100) surfaces indicate that for DMTe, the predominant adspecies, dimethyl tellurium, can be photodissociated to a metal adspecies at both 193 and 248 nm. For DMCd, the major adspecies, monomethyl cadmium, is unreactive to photon stimulation.

INTRODUCTION

Thermal and photon-assisted deposition processes involving organometallic precursor species are currently being investigated for II-VI and III-V compound semiconductors.[1] These processes provide the potential for reduced growth temperatures and increased process flexibility. Illustrations include reduced pressure laser assisted chemical vapor deposition (LCVD) of CdTe[2] and ultra high vacuum (UHV) metalorganic molecular beam epitaxy (MOMBE) of GaAs.[3] These relatively new deposition processes raise important questions concerning chemical mechanisms which must be answered if the processes and materials they produce are to be optimized.

This paper describes ongoing experimental studies[4,5] of the thermal and photon-induced surface reactions of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe). The objectives of these studies are to provide an understanding of the underlying chemical and physical processes and to explore novel approaches to CdTe heteroepitaxy. The work focuses on CdTe heteroepitaxy because of the importance of this material in electro optical systems.[6] DMCd and DMTe were the first precursor species selected for investigation because of their inherent scientific interest. The gas phase photochemistry of DMCd and DMTe has been extensively investigated; these molecules are known to undergo one photon dissociation to produce ground state metal atoms.[7-9] This behavior contrasts with that of trimethyl gallium and trimethyl arsenic which dissociate in the gas phase via a multiphoton excitation process.[10] The basic questions we attempt to answer in this study are: i) How do DMCd and DMTe interact with the surface of a substrate or growing thin film? and ii) Is this interaction such that single photon (as opposed to multiphoton) processes can be used to produce metal adspecies and, ultimately, epitaxial CdTe thin films?

EXPERIMENTAL

The experimental apparatus used in these studies is shown in Figure 1. It consists of a turbomolecular pumped, liquid nitrogen trapped UHV reaction cell interfaced to an ion/sublimation pumped UHV analysis chamber. The diagnostics used in these studies were X-ray photoelectron

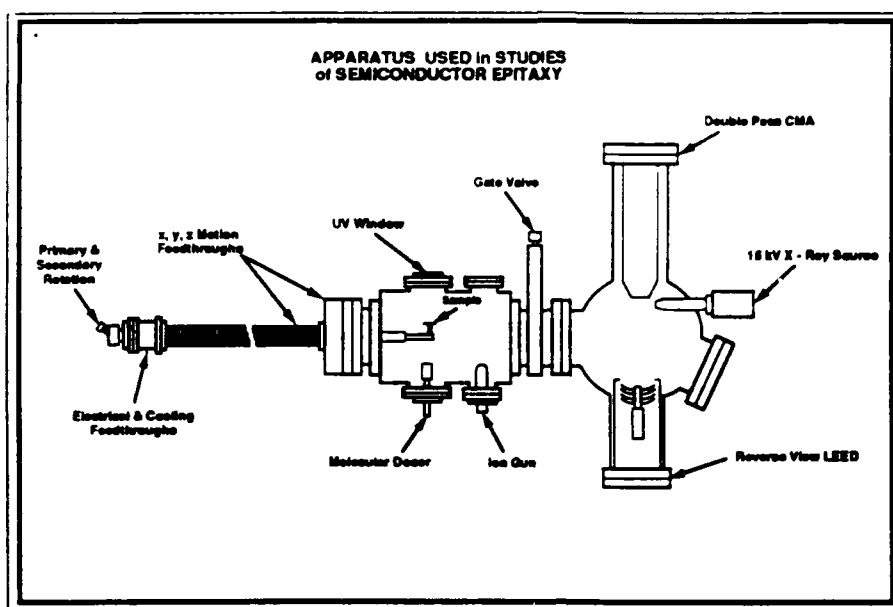


Figure 1. Schematic diagram of the experimental apparatus.

spectroscopy (XPS) and low energy electron diffraction (LEED). The sample was transferred between chambers using a linear motion feedthrough with sample heating (1200 K) and cooling (133 K) capabilities. Samples were exposed to reactive gas species using an effusive molecular beam doser. For the sample-source geometry used here, the angular distribution of the effusive beam produced only a nominal 10% variation in exposure over the analyzed area of the surface. Photon-induced processes were studied by irradiating the surface with UV photons produced by an excimer laser. These were introduced through a Conflat mounted MgF_2 window (Harshaw). The wavelengths used in these experiments were 193 nm and 248 nm. Laser fluence, controlled using a simple beam expander, ranged from 0.25 mJ cm^{-2} to 2.5 mJ cm^{-2} to minimize the effects of surface heating ($<3 \text{ K}$ to 30 K)[11].

The samples used in these studies were GaAs(100), Si(100), SiO_2 , and Au. The GaAs and Si samples were p-type electronic grade single crystal substrates provided by Litton and Monsanto, respectively. The SiO_2 sample was amorphous quartz, and the Au sample was a polycrystalline foil (Alfa Products). In situ sample cleaning involved Ar^+ ion etching at 1 kV. For the GaAs and Si surfaces, this was followed by annealing at 850 K[12] and 1100 K[13], respectively, to restore surface order. The DMCd and DMTe (Alfa), except where noted, were purified using a series of freeze-thaw cycles.

The XPS analyses were performed using a PHI 15 kV, Mg K_{α} source and a PHI double pass cylindrical mirror electron energy analyzer operated at a pass energy of 50 eV. The analyzer was calibrated using the Au $4f_{7/2}$ photoelectron peak at 83.8 eV. For the SiO_2 , sample charging effects were taken into account by referencing the spectra to the Si 2p peak at 103.4 eV. Adsorption coverages were calculated from known values of the X-ray mass absorption coefficients, electron mean free paths, and peak intensities using a technique developed by Madey, et al.[14]. Following Wedler and Klemperer,[15] reactive sticking coefficients were determined from the slope of plots of surface coverage versus exposure.

RESULTS

As discussed elsewhere[4], XPS analyses of the Cd and Te $3d_{5/2}$ peaks for adspecies on the various substrates led to the identification of three distinct binding energies for each peak. As an example, Figure 2 shows Cd $3d_{5/2}$ spectra for the Si(100) 2x1 surface exposed to DMCD at 133 K. The initial exposure produces a peak at 404.6 eV (FWHM = 2.0 eV) which corresponds well with Cd metal. At higher exposures, the spectrum is dominated by a monomethyl Cd (MMCd) peak at 405.2 eV. The details of how this surface reaction product distribution evolves with DMCD exposure are shown in Figure 3 where Cd adspecies coverage is plotted against DMCD exposure. From the slope of this plot, the reactive sticking coefficient of DMCD is found to be ~ 0.1 for the indicated conditions. Under similar conditions, DMTe is found to adsorb as the dimethyl and metal adspecies with Te metal representing a relatively minor component. The reactive sticking coefficient of DMTe on the Si(100) 2x1 surface was found to be ~ 0.5 at 133 K. Interestingly, while the saturation surface coverage for the Cd-adspecies at 133 K is ~ 0.7 monolayers, multilayer DMTe coverages may be produced.

Table 1 summarizes the adspecies which have been observed on the various substrates at 295 K[4] and 133 K. Where multiple adspecies are observed, the dominant species at high coverage/exposure is listed first. As indicated, measurements for SiO_2 and Au at 133 K are currently in progress. The measurements of DMTe adsorption on Si and SiO_2 at 295 K showed very limited uptake. This was originally attributed to a low DMTe sticking coefficient, but we are currently investigating the possibility that the DMTe used in the original measurements was contaminated by decomposition products.

Upon irradiation by 193 nm photons, no effect was observed for either the Cd or the Te metal adspecies. For the monomethyl adspecies, some desorption ($<50\%$) but no conversion to the metal was observed. For the dimethyl adspecies, conversion to the metal adspecies ($\sim 25\%$ to 75%) and some desorption ($<25\%$) were observed. The DMTe adspecies formed on Si and GaAs at 133 K were found to dissociate to metal adspecies with 248 nm photons. Studies using this wavelength have not been extended to other adspecies.

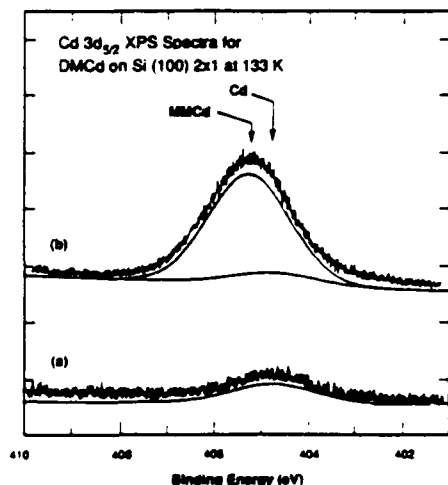


Figure 2. Cd $3d_{5/2}$ XPS spectra for the Si(100) 2x1 surface exposed at 133 K to a) $5 \times 10^{14} \text{ cm}^{-2}$ and b) $6 \times 10^{15} \text{ cm}^{-2}$ DMCD molecules.

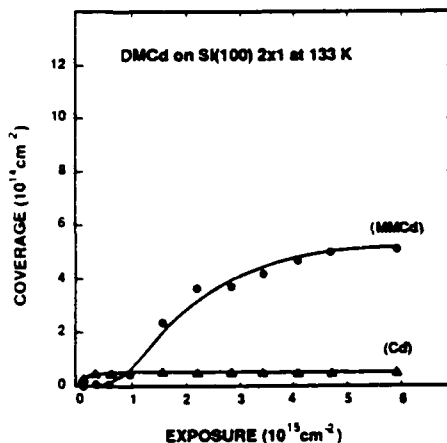


Figure 3. Plot of Cd adspecies surface coverage versus DMCD exposure for the Si(100) 2x1 surface at 133 K.

Table 1: Summary of Observed Adspecies^a

Substrate	Cd-Adspecies		Te-Adspecies	
	133 K	295 K	133 K	295 K
Si(100)	MMCd + Cd	MMCd	DMTe + Te	ND ^c
GaAs(100)	MMCd	MMCd	DMTe + Te	MMTe
SiO ₂	NA ^b	DHCd	NA ^b	ND ^c
Au	NA ^b	Cd	NA ^b	Te + DMTe

^aDominant species at high coverage/exposure listed first.

^bNA \equiv not available, measurement in progress

^cND \equiv no adspecies detected

The effects of photon irradiation on the dimethyl-adspecies is illustrated in Figure 4.[5] The lower spectrum shows the Te 3d_{5/2} XPS peak for Au exposed to DMTe at 295 K. The total adspecies coverage represented here corresponds to about 0.5 monolayers which is distributed between the metal (~60%) and dimethyl (~40%) peaks. The upper spectrum shows the effects of laser irradiation. Here it may be seen that ~80% of the dimethyl adspecies was converted to metal, ~5% was desorbed, and ~15% remained on the surface after irradiation. Further irradiation by an additional 5000 pulses did not eliminate the residual dimethyl adspecies.

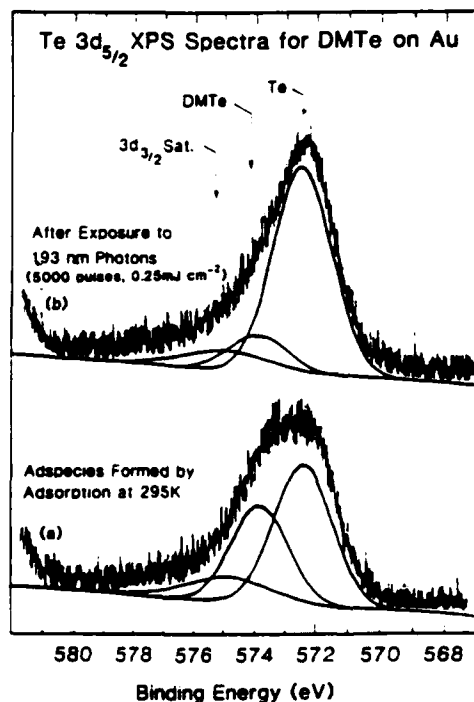


Figure 4. Te 3d_{5/2} XPS spectrum for DMTe adspecies on Au (a) before and (b) after irradiation by 5000 pulses of 193 nm laser light at 0.25 mJ cm⁻² per pulse. Each spectrum has been resolved into metal (572.6 eV) and a dimethyl (573.6 eV) peaks. The low intensity peak at 574.8 eV is an X-ray satellite associated with the Te 3d_{3/2} peak.

DISCUSSION

The thermal surface chemistry of DMCd and DMTe appears to be quite diverse. Disregarding the minor channel to form metal adspecies on Si and GaAs at 133 K (probably due to defect sites), DMCd appears to be more reactive than DMTe. Simple thermodynamic considerations might argue that this trend is due to the relatively weak average Cd-carbon bond strength, 36.2 kcal mole⁻¹ [7] compared to 57.5 kcal mole⁻¹ for DMTe [9]. On the other hand, substrate-metal bond strengths are probably stronger for Te than for Cd. Furthermore, the increased propensity for dissociation as the substrate changes from insulator to conductor does not follow any simple thermodynamic argument. We intend to pursue studies on single crystal quartz and gold substrates as well as n-doped semiconductors to further investigate this trend.

The photochemistry results are important for several reasons. First they demonstrate that species present on the surface in the dimethyl chemical state can be photodissociated. This finding is critical to the success of any CdTe deposition process based on laser induced surface chemistry of DMCd and DMTe. Studies now in progress will provide additional insight into the nature of these photon-assisted processes. Second, the photochemistry results also demonstrate clear differences in the behavior of the surface species we have assigned as dimethyl-, monomethyl-, and metal-adspecies. Further, the observed differences in behavior are the same for each metal alkyl. Thus, as a secondary result, the observed photochemistry helps to corroborate the peak assignments made on the basis of ligand shifts and bulk standards. In future work, we will add additional corroborating evidence obtained from thermal desorption measurements.

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REFERENCES

1. J.A. O'Neill, P. Shaw, E. Sanchez, Z. Wu and R.M. Osgood, Jr., "Surface Spectroscopic Studies of Organometallic Deposition," Mat. Res. Soc. Symp., this volume.
2. J.J. Zinck, P.D. Brewer, J.E. Jensen, G.L. Olsen and L.W. Tuh, Appl. Phys. Lett. 52, 1434 (1988); J.B. Mullin and S.J.C. Irvine, J. Vac. Sci. Technol. A4, 700 (1986)
3. E. Tokumitsu, Y. Kurow, M. Kanogai and K. Takahashi, J. Appl. Phys. 55, 3163 (1984).
4. C.D. Stinespring and A. Freedman, Chem. Phys. Lett 143, 584 (1988).
5. C.D. Stinespring and A. Freedman, Appl. Phys. Lett. 52, 1959 (1988).
6. R.A. Wood and R.J. Hager, J. Vac. Sci. Technol. A1, 1608 (1983).
7. C. Jonah, P. Chandra, and R. Bersohn, J. Chem Phys. 55, 1903 (1971), C.F. Yu, F. Youngs, K. Tsukiyama, R. Bersohn, and J. Preses, J. Chem. Phys. 85, 1382 (1986).
8. C.J. Chen and R.M. Osgood, J. Chem. Phys. 81, 327 (1984).
9. P.D. Brewer, J.E. Jensen, G.L. Olsen, L.W. Tutt and J.J. Zinck, Proc. Mat. Res. Soc. Symp. 101, 327 (1988); P.D. Brewer, Chem. Phys. Lett., 141, 301 (1987).

10. V.M. Donnelly, J.A. McCaulley, V.R. McCrary, C.W. Tu and J.C. Beggy, "Selective Area Growth of GaAs by Laser Induced Pyrolysis of Absorbed Gallium-Alkyls," Proc. Mat. Res. Soc. Symp., this volume.
11. D. Burgess, P.C. Stair, and E. Weitz, J. Vac. Sci. Technol. A4, 1362 (1986); P.C. Stair and E. Weitz, J. Opt. Soc. Am. B4, 255 (1987).
12. L.A. Kolodziejski, R.L. Gunshor, N. Otsuka, S. Datta, W.M. Becker and A.V. Nurmikko, IEEE J. Quantum Electron. QE-22, 1666 (1986).
13. M. Henzier, Surface Sci. 36, 109 (1973).
14. T.E. Mady, J.T. Yates and N.E. Erickson, Chem. Phys. Lett. 19, 487 (1973).
15. G. Wedler and W.F. Klemperer, Chemisorption: An Experimental Approach (Butterworths, London, 1976).

THERMAL AND PHOTON-INDUCED CHEMISTRY OF ADSORBED CADMIUM AND TELLURIUM ALKYLs

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ABSTRACT

Experimental studies of the thermal and photon-induced surface chemistry of two organometallic molecules, dimethyl cadmium and dimethyl tellurium, are reported for a variety of surfaces including Au, GaAs, Si, and SiO₂. These studies followed ultrahigh vacuum compatible procedures and used x-ray photoelectron spectroscopy to characterize the chemical state and coverage of the adspecies formed at 295 K. The results showed considerable diversity in the thermal surface chemistry of the systems investigated. Depending on the substrate, physisorption and dissociative chemisorption to yield monomethyl and metal adspecies were observed. Irradiation of the physisorbed adspecies with 193 nm UV photons led to single photon photodecomposition and limited photodesorption. Similar irradiation of the monomethyl-adspecies caused only limited photodesorption.

INTRODUCTION

The development of deposition techniques for III-V and II-VI compound semiconductors has been the goal of numerous studies reported in the recent literature. The techniques investigated include organometallic chemical vapor deposition (OMCVD)[1-3], laser-induced CVD (LCVD)[4-6], organometallic-molecular beam epitaxy (OM-MBE)[7], and molecular layer epitaxy (MLE)[8,9]. Although the deposition conditions encountered in each of these techniques are quite different, they all use organometallic molecules as the precursor or deposition species. Despite their importance, only limited information exists concerning the thermal and photon-induced surface chemistry of these molecules, and only recently have studies on this issue emerged[10-14].

This paper describes research aimed at determining the thermal and photon-induced surface chemistry of dimethyl cadmium (DMCd) and dimethyl tellurium (DMTe) on a variety of substrates. The goals of this research included the following: a determination of the identity of the adspecies formed by the interaction of the DMCd and DMTe with the substrate at 295 K, a measurement of the reactive sticking coefficients of DMCd and DMTe at 295 K, and a determination of the effects of 193 nm excimer laser generated photons on the identity and surface coverage of the adspecies.

EXPERIMENTAL APPROACH

The apparatus used in these studies consisted of an ultrahigh vacuum (UHV) surface analysis system and reaction chamber interfaced directly by a gate valve. Samples were transferred between the analysis chamber and reaction cell using a magnetically coupled linear transfer device[10]. GaAs(100), Si(100), SiO₂ or Au samples were exposed to the desired gas by backfilling the reaction chamber to pressures of 10⁻⁶ to 10⁻⁸ torr. The sample was then transferred to the adjacent chamber for analysis using x-ray photoelectron spectroscopy (XPS). The temperature of the sample was maintained at 295 K during the course of the reaction, and prior to

reaction, all samples were cleaned by Ar^+ ion etching (1 kV ion beam). The Si and GaAs substrates were also annealed at 1100 K and ~853 K, respectively, to remove ion-induced damage[15,16].

Photon-induced processes in the adsorbed species were studied by irradiating the surface through a reaction cell viewport (Suprasil) with 193 nm (6.4 eV) photons produced by a pulsed (15 ns) ArF excimer laser (Questek). The laser fluence was controlled using a two element beam expander which provided a low divergence beam.

RESULTS

The results of our XPS studies of the thermally induced surface chemistry of DMCD and DMTe at 295 K have been reported elsewhere[10]. Briefly, two key observations were made. First, the sticking coefficient of DMCD on GaAs was found to be $\sim 7 \times 10^{-3}$, while that of DMTe was more than two orders of magnitude smaller. Second, both metal alkyls, depending on the substrate, formed physisorbed and dissociatively chemisorbed adspecies. These adspecies, for each substrate, are summarized in Table 1. Because of limited DMTe uptake on Si and SiO_2 , no data for tellurium adspecies on these surfaces were obtained.

Both the physically adsorbed DMCD and DMTe molecules as well as the monomethyl cadmium and monomethyl tellurium adspecies could, in principle, be further decomposed by irradiation with UV photons. To investigate this possibility, these adspecies were exposed to 193 nm radiation produced by the excimer laser. The energy fluence per 15 ns pulse was typically 0.25 mJ cm^{-2} however, some exposures at 2.5 mJ cm^{-2} were also performed. At 0.25 mJ cm^{-2} multiphoton processes are not likely, and the maximum surface temperature rise, 3 K, is well below that needed to induce thermal surface processes. The results of these studies will be reported in more detail elsewhere[11] and are summarized in Table 1.

Typical results for tellurium adspecies on Au are illustrated in Figure 1. The lower spectrum shows the Te $3d_{5/2}$ XPS peak for Au exposed to $4 \times 10^{17} \text{ cm}^{-2}$ DMTe molecules at 295 K, while the upper spectrum shows the effect of irradiating these adspecies with 5000 pulses of 193 nm photons at a fluence of 0.25 mJ cm^{-2} . The decrease in intensity of the physisorbed DMTe peak and corresponding increase in intensity of the metal peak indicates that essentially all of the physisorbed adspecies are photo-decomposed.

For physically adsorbed DMCD on SiO_2 , similar XPS analyses showed that, after exposure to 5000 pulses of 193 nm radiation at an energy density of 0.25 mJ cm^{-2} , approximately 80% of the DMCD molecules were photodesorbed, while 20% were photodissociated to form Cd metal. Exposure to an additional 5000 pulses produced no further changes in the spectra.

Table 1 - Summary of Adspecies and Photo Effects

Substrate	Adspecies	Photo Effect @ 193 nm
Au	Cd (CH_3) ₂ Te + Te	None Decomposition to Te
GaAs(100)	(CH_3)Cd (CH_3)Te + Te	Partial Desorption Partial Desorption
Si(100)	(CH_3)Cd	Partial Desorption
SiO_2	(CH_3) ₂ Cd	Partial Desorption Decomposition to Cd

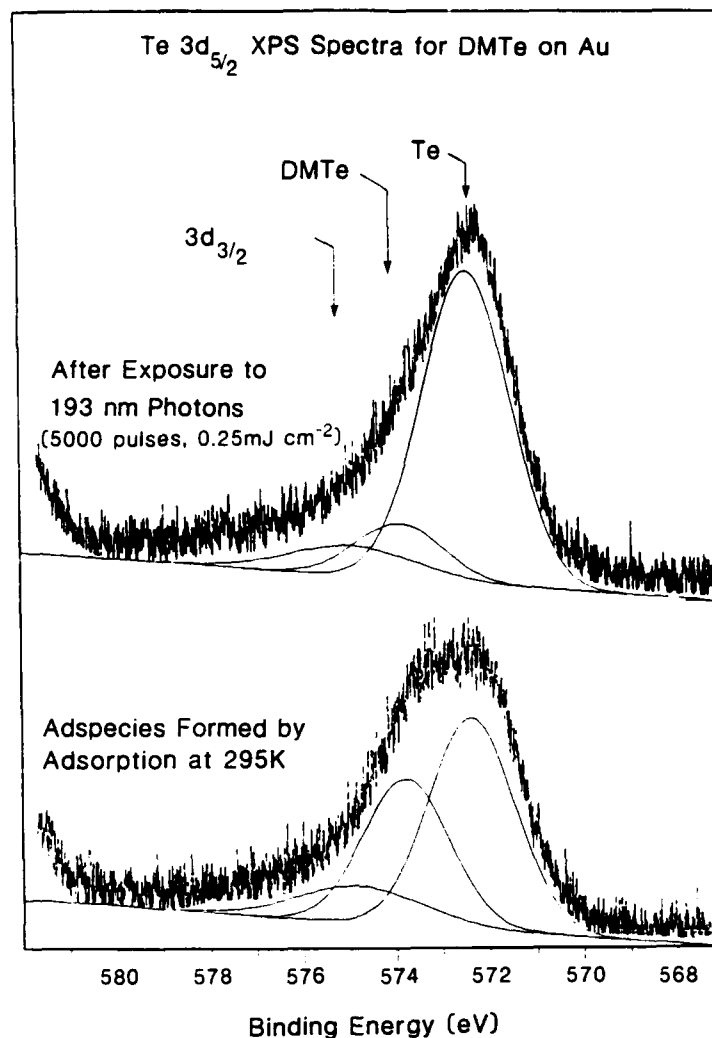


Figure 1. Te $3d_{5/2}$ XPS spectra for Au exposed to 4×10^{17} DMTe cm^{-2} at 295 K before (lower spectrum) and after exposure to 5000 pulses of 193 nm radiation at 0.25 mJ per 15 ns pulse. These spectra have been resolved into metal (572.6 eV) and DMTe (573.6 eV) components. The low level peak at 574.8 eV is an x-ray satellite associated with the Te $3d_{3/2}$ peak (not shown).

Laser irradiation of the monomethyl Cd adspecies observed on the GaAs and the Si surfaces produced only partial photodesorption. Exposure to 5000 pulses of 193 nm radiation at 0.25 mJ cm^{-2} desorbed approximately 50% of the monomethyl adspecies; however, no changes in chemical state of the adspecies were observed. Similar results were observed for the monomethyl Te adspecies on the GaAs surface.

CONCLUSIONS

The results of this study provide two important observations concerning the thermal surface reactions of DM Cd and DMTe at 295 K on GaAs(100), Si(100), Au, and SiO_2 . The first is the adspecies identities and the second concerns the reactive sticking coefficients. As reported elsewhere, insight into these results is provided by an understanding of molecular structure of the DM Cd and DMTe molecules and the potential interactions of this structure with each surface[10]. Briefly, DMTe is a closed shell molecule and must initially interact at close range with the surface through lone pair electrons on the Te atom. DM Cd, however, has

three empty low-lying p orbitals available for accepting electrons from the substrate. Although both interactions can lead to stable adspecies, these considerations are consistent with the observation of larger sticking coefficients for DMCd. Moreover, the dissociative chemisorption of DMCd on GaAs, Si, and Au and physisorption on SiO₂ are consistent with the enhanced probability of electron transfer for metal and semiconductor surfaces relative to that for insulators. The results also show that physisorbed adspecies may be photodissociated using 193 nm radiation, while the monomethyl-adspecies are not. The former observation is consistent with the results of corresponding studies of the gas phase photochemistry of DMCd[17,18]. Moreover, gas phase studies for monomethyl cadmium suggest that relatively strong absorption bands in the 284 nm region may more efficiently dissociate the monomethyl-adspecies.

A complete understanding of the thermal and photon-induced processes discussed here will require more detailed study of the effects of key parameters, surface orientation, structure, and temperature as well as laser wavelength and fluence, on the surface chemistry involved. Because of the importance of metal alkyl-surface interactions in various thermal and photon-assisted deposition processes studies of these effects are clearly warranted and are planned for the near future.

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REFERENCES

1. M.J. Ludowise, J. Appl. Phys. 58, R31 (1985).
2. R.D. Dupuis, Science 226, 623 (1984).
3. P.D. Lee, D. McKenna, D. Kapur, and K.F. Jensen, J. Crystal Growth 77, 120 (1986).
4. D.J. Erlich and R.M. Osgood, Jr., Chem. Phys. Lett. 79, 381 (1981).
5. V.M. Donnelly, V.R. McCrary, A. Appelbaum, D. Brasen, and W.P. Lowe, J. Appl. Phys. 61, 1410 (1987).
6. R.R. Krchnavek, H.H. Gilgen, J.C. Chen, P.S. Shaw, T.J. Licata, and R.M. Osgood, J. Vac. Sci. Technol. B5, 20 (1987).
7. E. Tokumitsu, Y. Kurou, M. Kanogai, and K. Takahashi, J. Appl. Phys. 55, 3163 (1984).
8. J. Nishizawa, H. Abe, and T. Kurabayashi, J. Electrochem. Soc. 132, 1199 (1985) and J. Electrochem. Soc. 132, 1939 (1985).
9. J. Nishizawa, K.T. Kurabayashi, H. Abe, and N. Sakurai, J. Vac. Sci. Technol. A4, 706 (1986).
10. C.D. Stinespring and A. Freedman, Chem. Phys. Lett., to be published.
11. C.D. Stinespring and A. Freedman, to be published.
12. G.S. Higashi, L.J. Rothberg, and C.C. Fleming, Chem. Phys. Lett. 115, 167 (1985).
13. E.D.B. Bourdon, J.P. Cowin, I. Harrison, J.C. Polanyi, J. Segner, C.D. Stanners, and P.A. Young, J. Phys. Chem. 88, 6100 (1984).
14. F.L. Tabares, E.P. Marsh, G.A. Bach, and J.P. Cowin, J. Chem. Phys. 86, 738 (1987).
15. M. Henzler, Surface Sci. 36, 109 (1973).
16. L.A. Kolodziejski, R.L. Gunshor, N. Otsuka, S. Datta, W.M. Becker, and A.V. Nurmikko, IEEE, J. Quant. Electron. QE-22, 1666 (1986).
17. C.J. Cheng and R.M. Osgood, J. Chem. Phys. 81, 327 (1984).
18. J.O. Chu, G.W. Flynn, C.J. Chen, and R.M. Osgood, Jr., Chem. Phys. Lett. 119, 206 (1985).